PB-230 351

ADSORPTION OF SURFACTANTS ON SELECTED MINERALS

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31 August 1966

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TERMINAL REPORT ON FEDERAL WATER POLLUTION CONTROL ADMINISTRATION GRANT No. WP 00611-01 (02) "ADSORPTION OF SURFACTANTS ON SELECTED MINERALS"

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Grant Period: June 1, 1964 - Aug. 31, 1966

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SUMMARY STATEMENT

The Division of Water Supply and Pollution Control Grant WP 00611-01 (02) "Adsorption of Surfactants on Selected Minerals" was initiated to study the conditions under which certain alkyl surfactants are adsorbed on typical rock and/or soil minerals. In the initial proposal a grant period of three years had been requested. However, the time period was shortened to two years by the Division of Water Supply and Pollution Control.

It was expected that adsorption on several minerals such as kaolinite, quartz, a feldspar and perhaps calcite would be studied. It was hoped that effect of pH, other organics, and some inorganics on this adsorption might also be studied.

Adsorption on only one mineral, kaolinite, was actually studied during the grant period. Only one mineral was studied because it was soon realized, after starting the research work, that meaningful results only could be obtained if one or at the most two minerals were studied in depth. Kaolinite was selected for study because of its common occurrence and because it appears to be the simplest of the clay minerals.

Some research work was done on quartz but this work was done for calibration purposes and study of surfactants used.

During the period of the grant several lines of investigation were followed. These different lines could be designated as subprojects. The subprojects were:

1) Adsorption of alkyl surfactants on kaolinite in the absence of contaminants and pH drift studies in the same systems.

2) Adsorption of alkyl surfactants on kaolinite in the presence of a long chain alcohol and a condensed phosphate.

3) Streaming potential study of kaolinite and quartz.

4) Streaming potential and microelectrophoresis study of kaolinite in

the presence of alkyl surfactants.

5) Infrared study of the adsorption of alkyl surfactants on kaolinite.

6) Contact angle study of the effect of surfactant configuration on adsorption of surfactants.

Thus, although only one mineral was studied it was studied in considerable depth and much was learned regarding adsorption of alkyl surfactants on it.

RESULTS OF THE INVESTIGATIONS

Adsorption of Alkyl Surfactants onto Kaolinite in the Absence of Contaminants and pH Drift Studies in the Same Systems

In this subproject the adsorption of two typical anionic and two typical cationic surfactants onto kaolinite was studied. For this subproject and all others the kaolinite selected for study was from Lewistown, Montana and was obtained from Wards Natural Science Establishment, Inc. (kaolinite No. 17). Infrared and x-ray diffraction studies of the material indicated that it was a high-grade kaolinite with few impurities. It had a specific surface of 13.1 M^2/gm as determined by nitrogen adsorption.

The anionic surfactants studied were sodium dodecylsulfate (SDS), a high purity material obtained from the U.S. Department of Agriculture, Agricultural Research Service and linear sodium dodecylbenzenesulfonate (SDBS) about 97% pure, obtained from Stepan Chemical Company. The cationic surfactants studied were trimethyldodecylammonium chloride (TDAC), a +99.5% pure material obtained from Lachat Chemical Company and dodecylammonium chloride (DAC), a high purity material obtained from Armour Industrial Chemical Co. pH was raised or lowered by reagent grade NaOH or HCl addition. Water used was first distilled and then redistilled in a pyrex redistiller.

Adsorption tests were carried out in 30 ml glass bottles. For each test 0.45 gm of clay was placed in a glass bottle. Next, 25 ml of surfactant solution of proper pH was transferred to the bottle. The bottle was then agitated for 72 hours. Also, 25 ml of the same surfactant solution was placed in an empty bottle and agitated for 72 hours. After agitation and a settling period, a quantity of the clear liquid over the clay was withdrawn for colorimetric analysis. If the clay failed to settle out quickly, the sample was centrifuged. At the same time a similar quantity of liquid was

withdrawn from the "blank" for analysis. The exact quantities of liquid withdrawn for analyses depended on approximate concentrations of surfactants and were chosen so that the colorimetric analyses were performed at near optimum points on calibration curves. For the anionic surfactant analyses the methylene blue technique of Jones[1] was used. For the cationic surfactants the bromophenol blue technique of Mukerjee and Mukerjee[2] was used. Adsorption was taken as the difference in surfactant solution concentration between the clay containing sample and the "blank" sample. Equilibrium concentration was taken as the final solution concentration of surfactant in the clay containing sample. Initial pH of the surfactant solution was measured as was also the final pH of both the clay containing sample and the "blank." Temperatures during the tests ranged from 24-28°C.

Results

Figure 1 shows adsorption as a function of final surfactant concentration for SDS, for a number of pH values. Both initial and final pH values (pH_i and pH_f) are indicated. Also shown on this figure is a curve from Iwasaki, et al[3] for SDS adsorption at pH 3. Figure 2 shows similar data for SDBS. Figure 3 shows adsorption as a function of final surfactant concentration for the TDAC for various pH values. Figure 4 shows similar data for DAC. Also shown on this figure is a curve from Iwasaki, et al[3] for DAC adsorption at pH 6.

Discussion of Results

In general the data of Figure 1 show that the lower the equilibrium pH, the greater the adsorption of SDS. In fact for initial pH 2.7 and equilibrium pH 3.9 there is quite strong adsorption onto kaolinite. This phenomenon would be expected considering the probable considerable anionic exchange

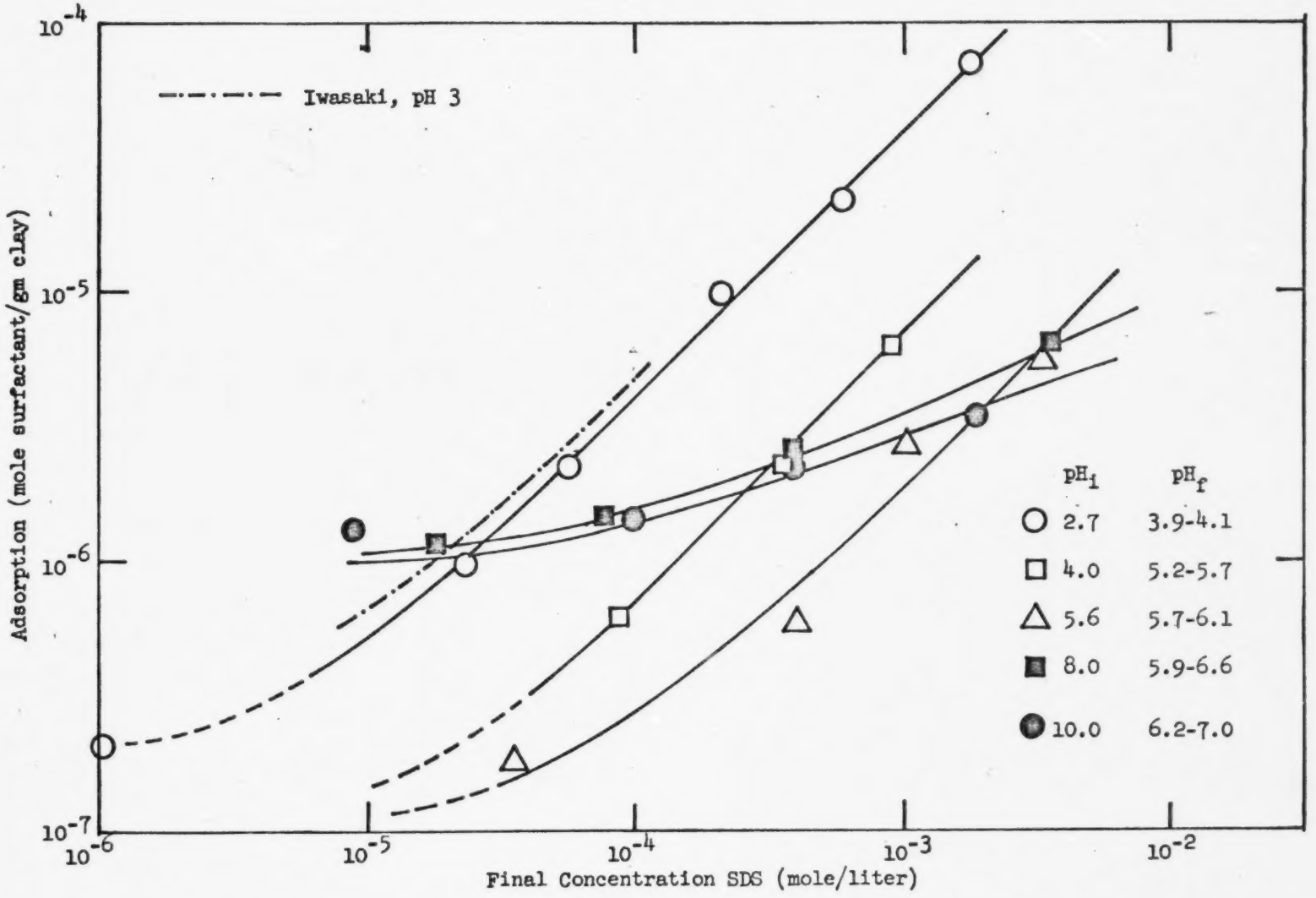

Figure 1. Adsorption of SDS onto Kaolinite as a Function of Final SDS Concentration

capacity of kaolinite[4] and the presence of positive charges on kaolinite edges[5,6] which would tend to be available for anionic adsorption at low pH values. At higher pH values these positive aluminum sites should adsorb OH radicals and become neutral and even negative in character[6]. The adsorption of the anionic surfactant at initial pH 8 - 10 does not fit into this reasoning. This relatively good adsorption may be the result of activation caused by a low level of heavy metal contamination. However, the very small quantities of impurities present in the kaolinite studied do not tend to confirm this thought.

Figure 2 in general tends to confirm the findings of Figure 1 except that the anomaly around pH_i 8 - 10 is not in evidence. Thus most of the unexpected results of Figure 1 must be attributed to some property of the SDS used.

Note that both Figures 1 and 2 indicate a large anion exchange capacity for the Montana kaolinite.

The adsorption curves of Figure 3 illustrate well how cationic adsorption on kaolinite is increased with increasing pH up to some equilibrium pH above pH 10. Note, however, that when final pH is increased to pH 13 adsorption is less at relatively low surfactant concentrations. That adsorption is still high at higher concentrations of TDAC would seem to indicate that surfactant adsorption in this pH region, and therefore high Na^+ ion concentration, is hindered mainly by a competition between Na^+ ion and amine ion.

From Figure 4 it appears that there is somewhat more adsorption of DAC onto kaolinite at higher surfactant concentrations than of TDAC. This illustrates the principle that a surfactant that hydrolyzes will in general adsorb in greater quantities than surfactants that do not. It is believed that the molecular species present because of hydrolysis will tend to aid adsorption

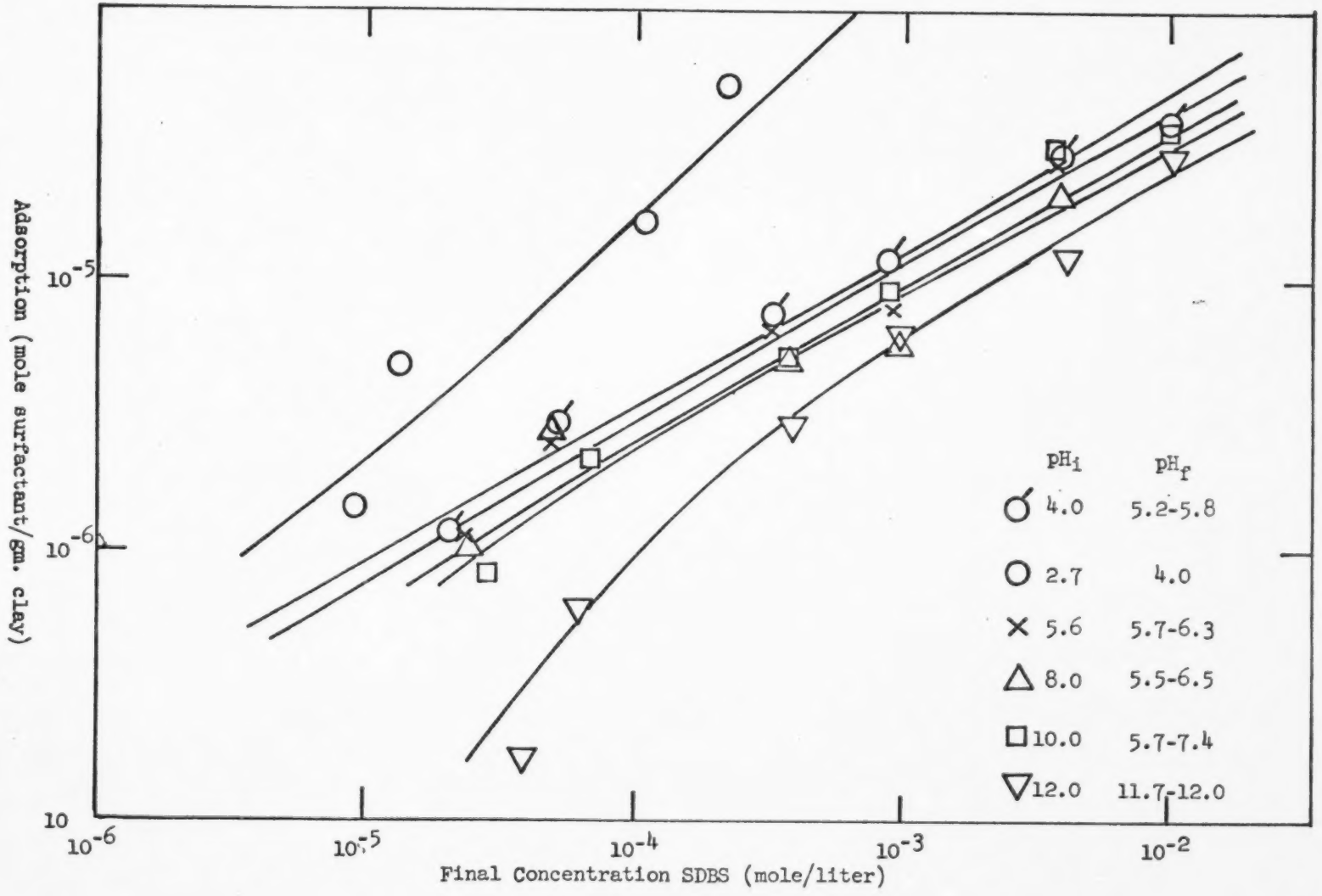

Figure 2. Adsorption of SDBS onto Kaolinite as a Function of Final SDBS Concentration

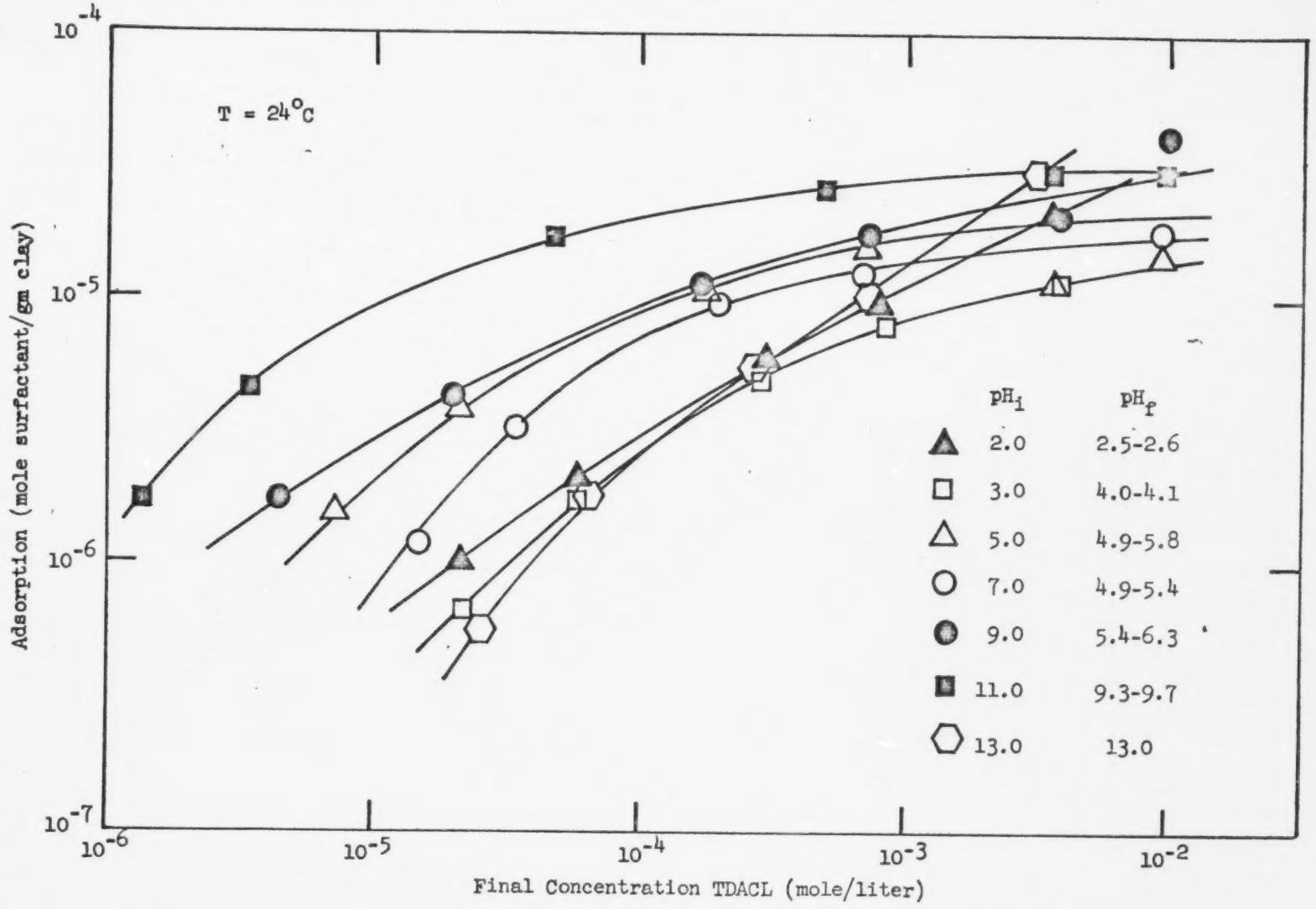

Figure 3. Adsorption of TDACL onto Kaolinite as a Function of Final TDACL Concentration

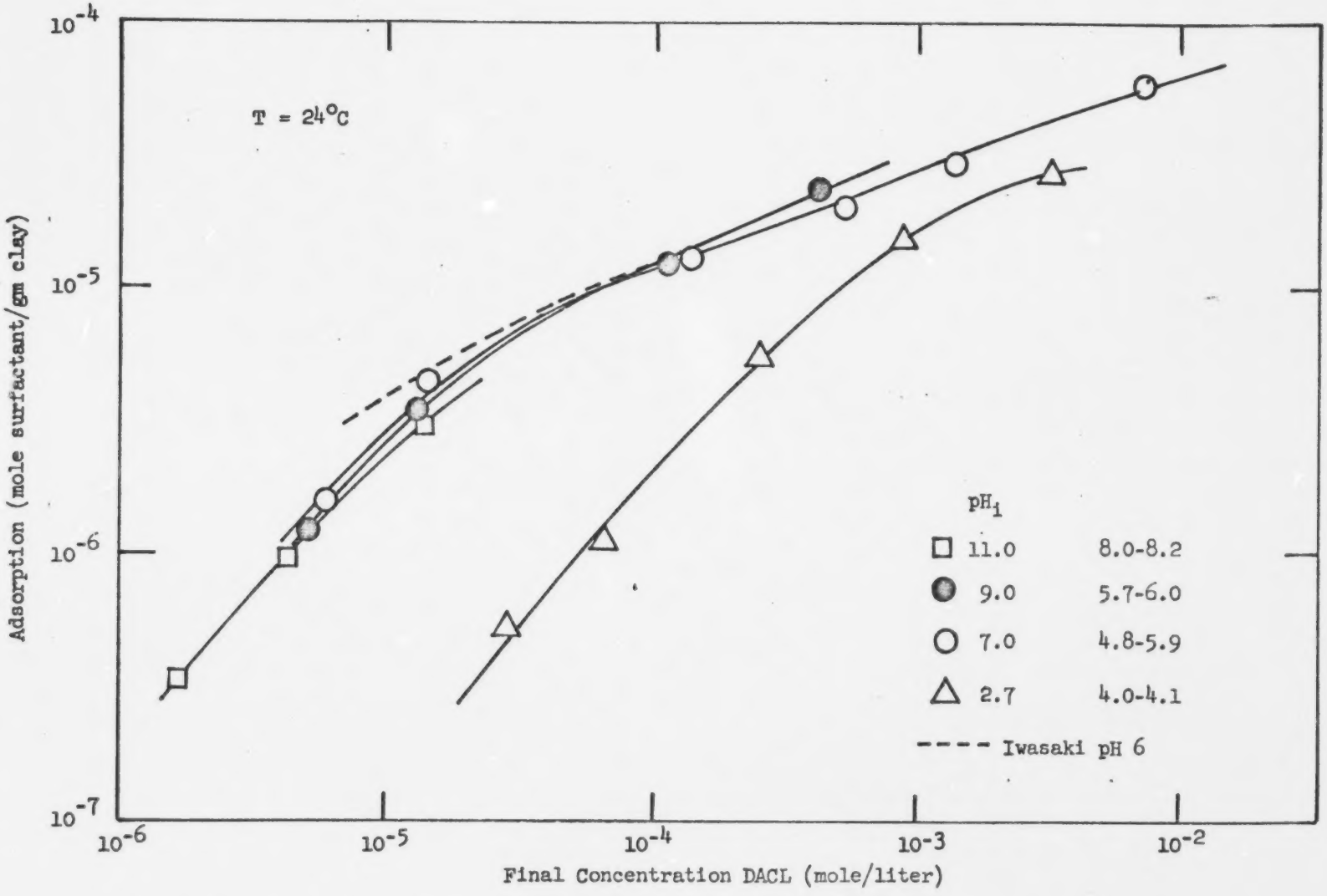

Figure 4. Adsorption of DACL onto Kaolinite as a Function of Final DACL Concentration

by screening repulsion between like charged ionic heads[7,8].

An interesting thing that can be observed from a comparison of Figures 1, 2, 3 and 4 is that the shapes of the anionic and cationic adsorption curves are quite different. The anionic curves do not appear to level off as surfactant concentration is increased while the cationic curves (particularly those for the quaternary amine) tend to do so. It is also interesting to note that for TDAC the curve for an equilibrium pH 9.5 appears to level off at an adsorption value around 3×10^{-5} mole surfactant/gm clay. This value would indicate a cation exchange capacity of about 3 mequiv/100 gm clay, a typical value for a kaolinite[4]. The curves for SDS and SDBS particularly for pH_i 2.7 indicate that the ultimate anion exchange capacity for this particular kaolinite is greater than the cationic exchange capacity.

pH Drift Studies

During the course of the adsorption experiments it was noted (as can be seen from data on Figures 1 - 4) that above neutrality the pH of the various solutions drifted with time toward a lower pH value. At acid pH values the pH drifted toward higher pH values. The drift was rapid during the first hour following the placing of a solution in one of the glass bottles used in the adsorption experiments. After one hour the drift was slower and in all cases ceased after 20 hours.

It was found that part of the drift could be attributed to the presence of the kaolinite and part to the glassware. Figure 5 shows pH drift for the glassware plus kaolinite, for the glassware alone and for kaolinite alone. The kaolinite alone values were obtained by subtracting glassware alone values from glassware plus kaolinite values. No surfactant was present in the tests of this figure. Figure 6 shows the effect of the presence of surfactant on the

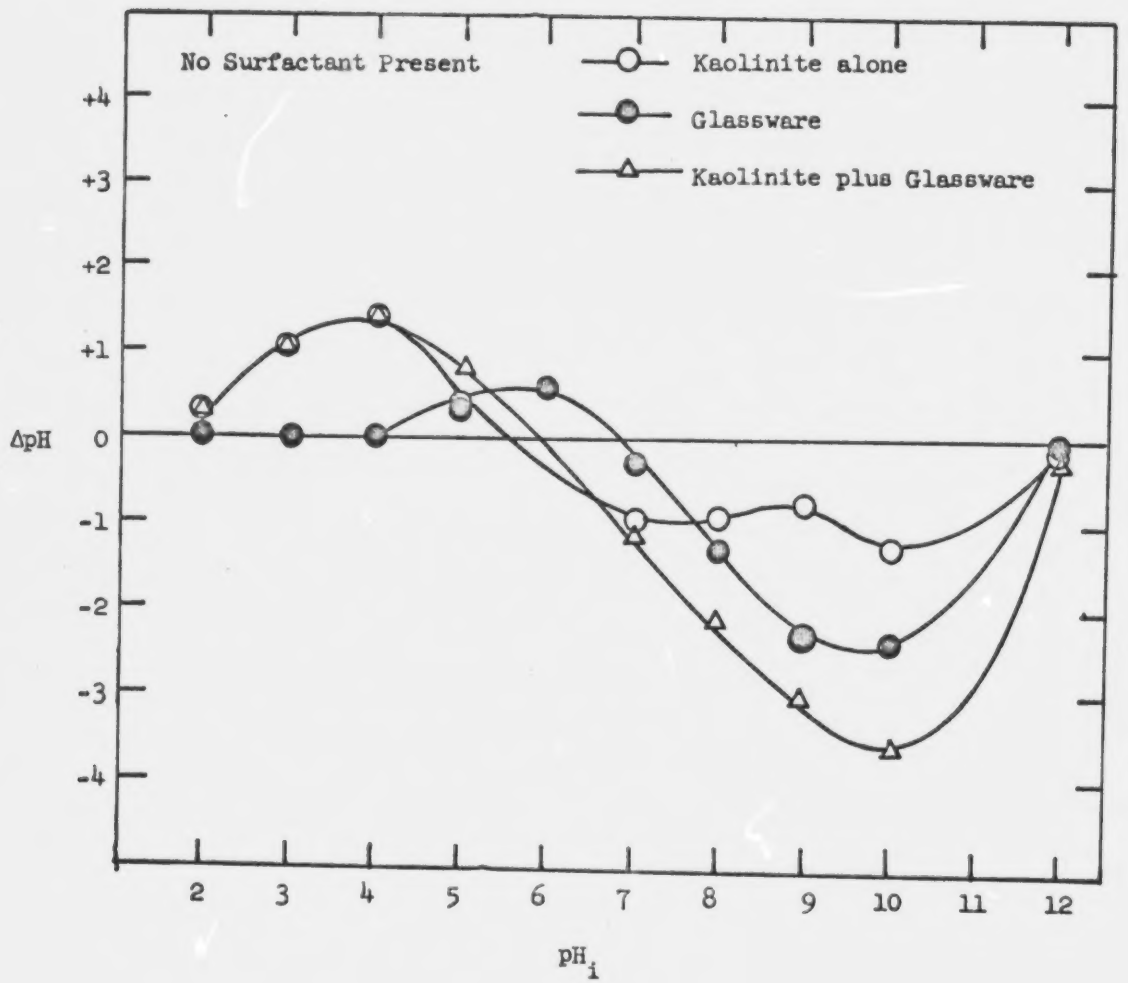

Figure 5. pH Drift Curves for Kaolinite and Glassware - No Surfactant Present

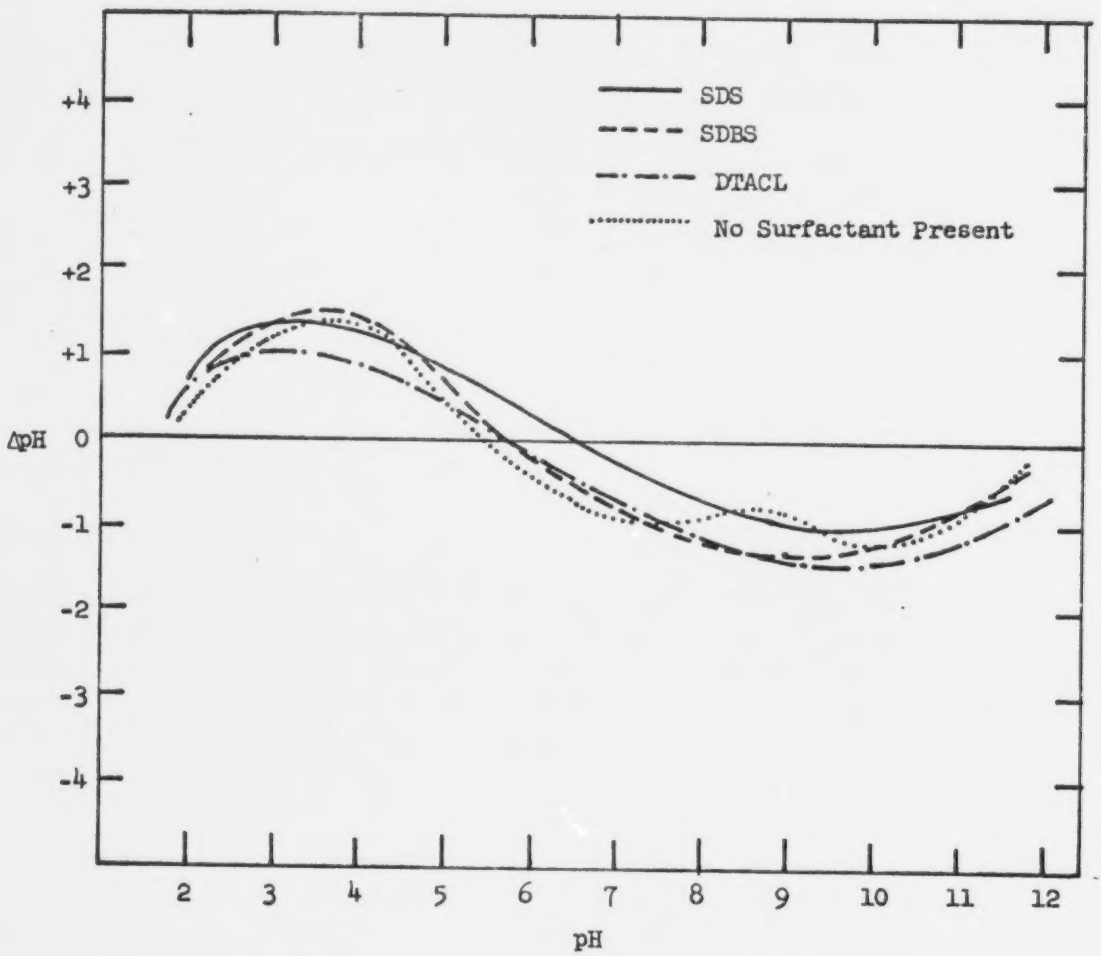

Figure 6. pH Drift Curves for Kaolinite - Various Surfactants Present

pH drift due to kaolinite. The data of this figure are from averages of several concentrations (10^{-5} to 10^{-3} M) of the surfactants.

Additional work on the topic of pH drift is continuing at the South Dakota School of Mines and Technology under another financial source.

Adsorption of Ionic Alkyl Surfactants on Kaolinite in the Presence of a Long Chain Alcohol and a Condensed Phosphate

The effects of addition of either a long chain alcohol or a condensed phosphate on adsorption of sodium dodecylsulfate (SDS) and trimethyldodecylammonium chloride (TDAC) onto kaolinite were investigated. The general procedure for adsorption measurements previously outlined were employed for these studies. The same chemicals were used as before plus sodium hexametaphosphate obtained from Monsanto Chemical Company and reagent grade decyl alcohol obtained from Matheson, Coleman and Bell. The temperature range for the tests was 24-27°C.

Effect of Alcohol Addition

Figure 7 shows an example of the effect of addition of 2.3×10^{-4} M decyl alcohol (a saturated solution) on adsorption of both SDS and TDAC. This figure is for final ionic alkyl surfactant concentrations of 10^{-4} M and shows adsorption of ionic surfactant as a function of initial pH. Curves are shown for adsorption both with and without alcohol addition. The figure shows clearly that the presence of the alcohol aids adsorption of both anionic and cationic surfactants. The enhancement is particularly marked between pH_i 4 and 8 for the case of the anionic surfactant. The only condition under which there appears to be little or no enhancement is at relatively high pH_i values for the anionic surfactant system. For the cationic system significant enhancement appears to take place over the entire pH_i range studied. It is deduced that the alcohol functions at least in good part by screening like

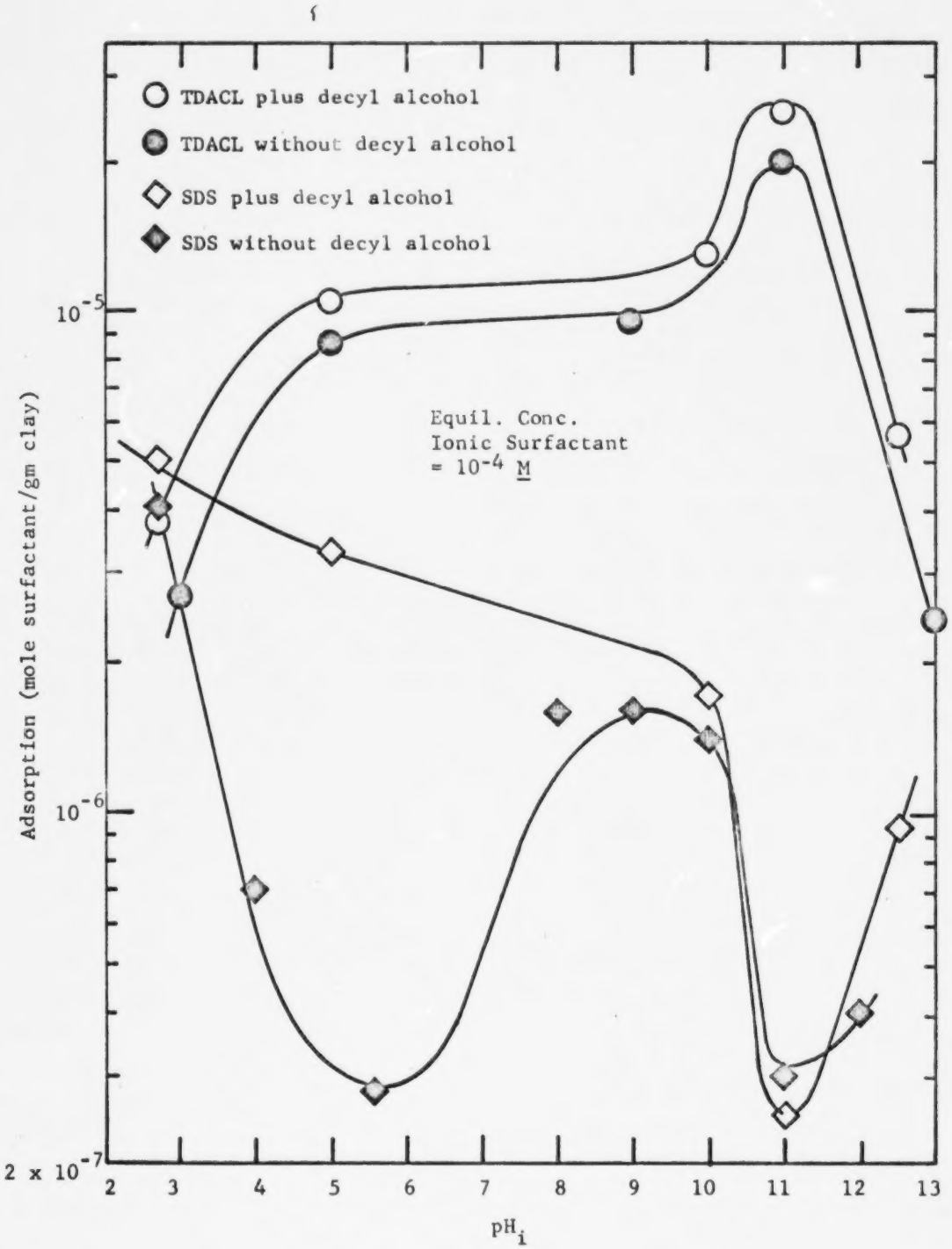

Figure 7. Effect of Decyl Alcohol on Adsorption of Ionic Alkyl Surfactants onto Kaolinite, Adsorption versus pH_i

charged heads of surfactant ions. Thus, it should be easier for surfactant ions to associate near the surface (if their tendency to repel each other is partly overcome by alcohol molecules fitting between charged ions).

Considering the especially large adsorption enhancement at pH_i values between 4 and 8 in the SDS system, this increased adsorption must be related to the overall negative charge on the kaolinite plus the ability of the alcohol to screen ionic heads. Around pH_i 5, for example, if no alcohol is present there is a fair amount of adsorption on positive kaolinite edge sites plus also on some face sites. However, an individual ion will probably adsorb on the face only if it can find an aluminum site that is neutral or positive (the overally negative face tends to repel the SDS anions.) Of course, a reasonable quantity do appear to adsorb since apparently the aluminum sites often act like such sites in corundum (at which pH the sites would generally be positively charged). This can be seen from Figures 1 and 2, which show very good SDS and SDBS adsorption possible at acid pH values if sufficient surfactant is present. The addition of the alcohol should help association of ions into so called hemimicelles[7,9]. Hemimicelles are associations of alkyl ions or dipoles in the two dimensional realm of the surface similar to micelles in bulk solution. They form when critical micelle concentration within the double layer has been exceeded, which may be at bulk concentrations much below the critical micelle concentration. The long hydrocarbon chains in the hemimicelles point out from the solid surface. At any rate, the whole "hemimicelle" composed of many ions should tend to adsorb at one of the neutral or positive aluminum sites. Obviously overall surfactant adsorption would be greatly increased.

That better adsorption in the absence of the alcohol is found at lower

pH values ($pH_i \sim 2.7$) tends to confirm the "hemimicelle" hypothesis since the kaolinite surface should be less negative at this pH, at least according to microelectrophoresis work done on the subproject on zeta potential of kaolinite.

Figure 8 is similar to Figure 7 except that pH_f is plotted rather than pH_i. The curves of this figure are somewhat more compressed and the anionic and cationic curves cross at a higher pH value. The crossing of the several curves near pH 4 indicate that this pH may be a ZPC of the kaolinite studied, a considerably higher value than indicated by streaming potential and microelectrophoresis work[6,10].

Effect of Addition of a Condensed Phosphate

Figures 9, 10 and 11 show the effect of addition of sodium hexametaphosphate on adsorption of SDS. At pH_i values less than neutral typically the addition of a small quantity of the condensed phosphate increased adsorption of SDS. At greater phosphate concentrations the adsorption dropped off, particularly for pH_i 2.7. At pH_i values above neutrality the adsorption of SDS tended to drop with small phosphate additions, then increased with increasing phosphate concentration to some point above which it again dropped. Several competing things may be taking place. One item has to do with the phosphate dispersing the clay creating more adsorption sites. The other has to do with the phosphate adsorbing and making the kaolinite surface much more negative. Also it should be noted that pH_f value increased as phosphate addition increased.

Figures 12, 13, and 14 show the effect of sodium hexametaphosphate addition on adsorption of TDAC. At all pH_i values increasing addition of

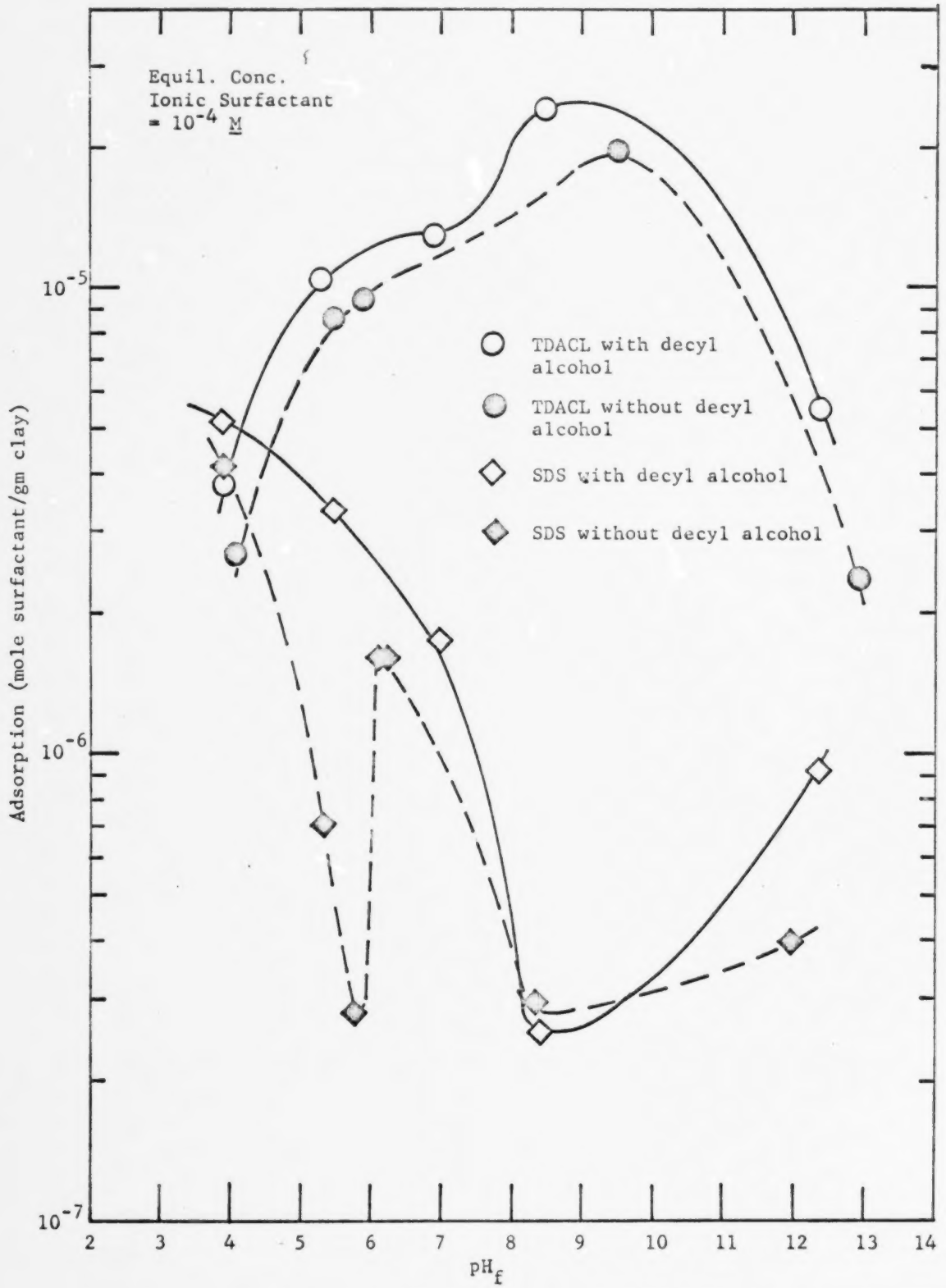

Figure 8. Effect of Decyl Alcohol on Adsorption of Ionic Alkyl Surfactants onto Kaolinite, Adsorption versus pH_f .

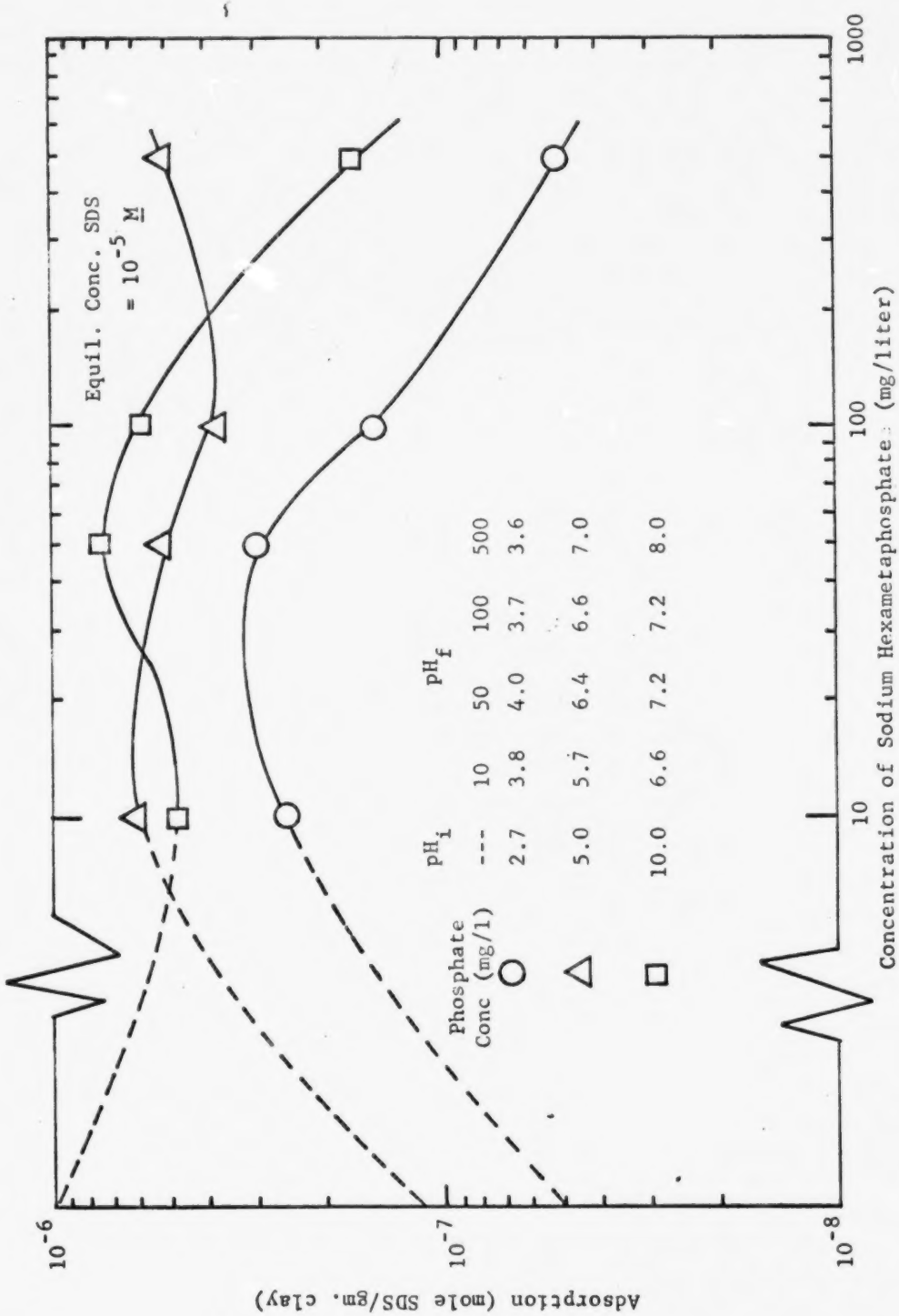

Figure 9. Effect of Sodium Hexametaphosphate on Adsorption at 10^{-5} M SDS

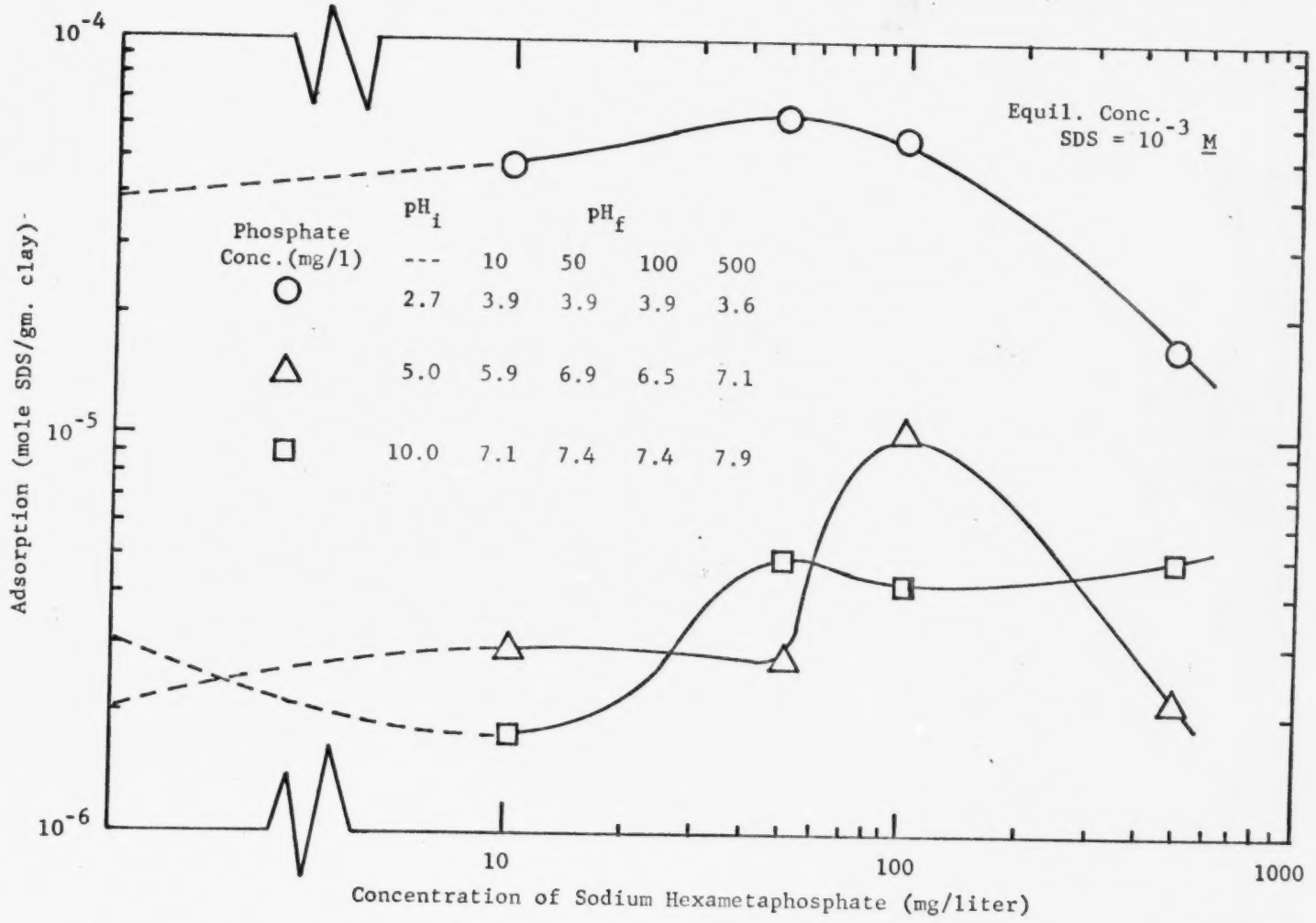

Figure 10. Effect of Sodium Hexametaphosphate on Adsorption of SDS at 10^{-3} M SDS

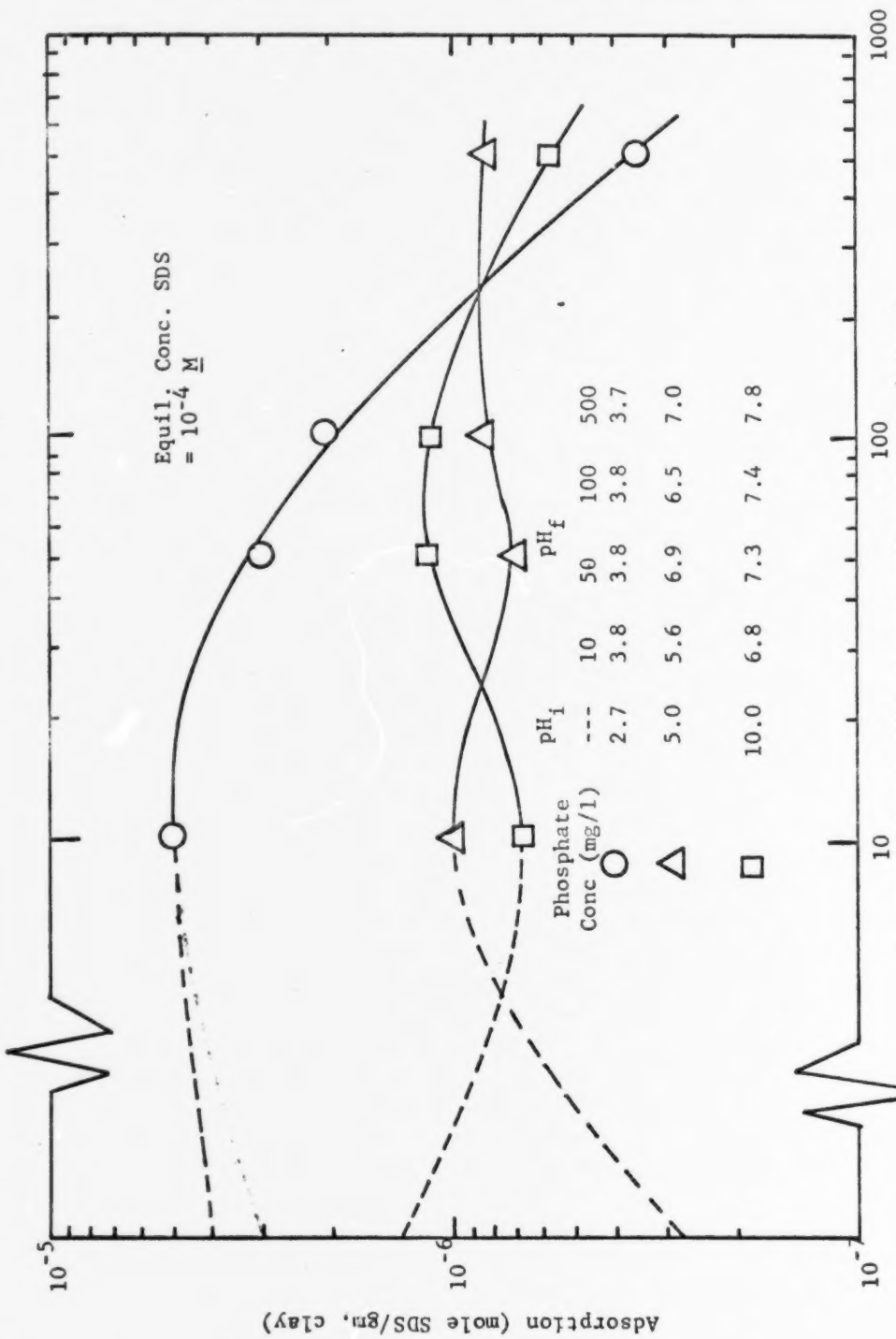

Figure 11. Effect of Sodium Hexametaphosphate on Adsorption at 10^{-4} M SDS

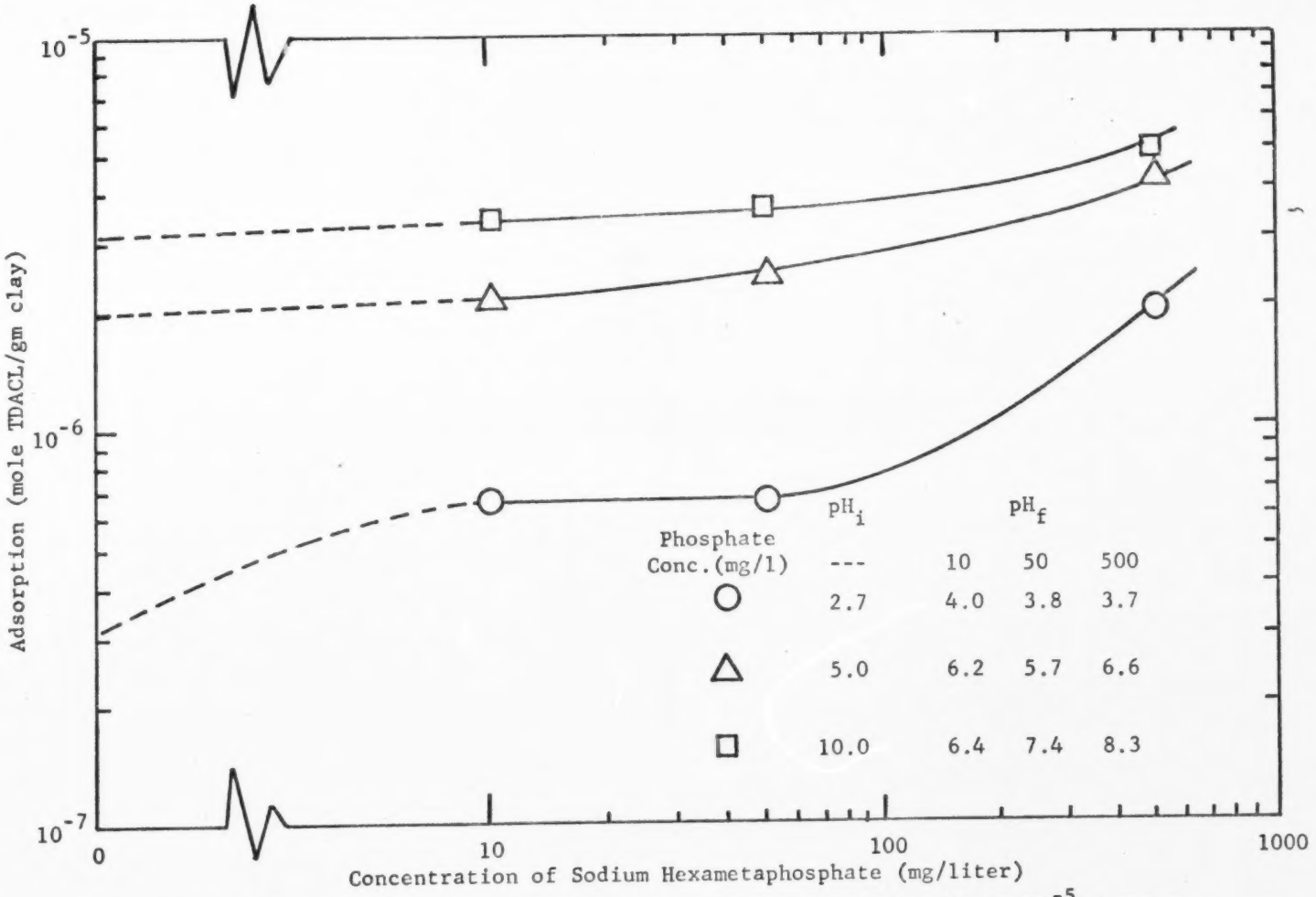

Figure 12.Effect of Sodium Hexametaphosphate on Adsorption of TDACL at 10^{-5} M TDACL

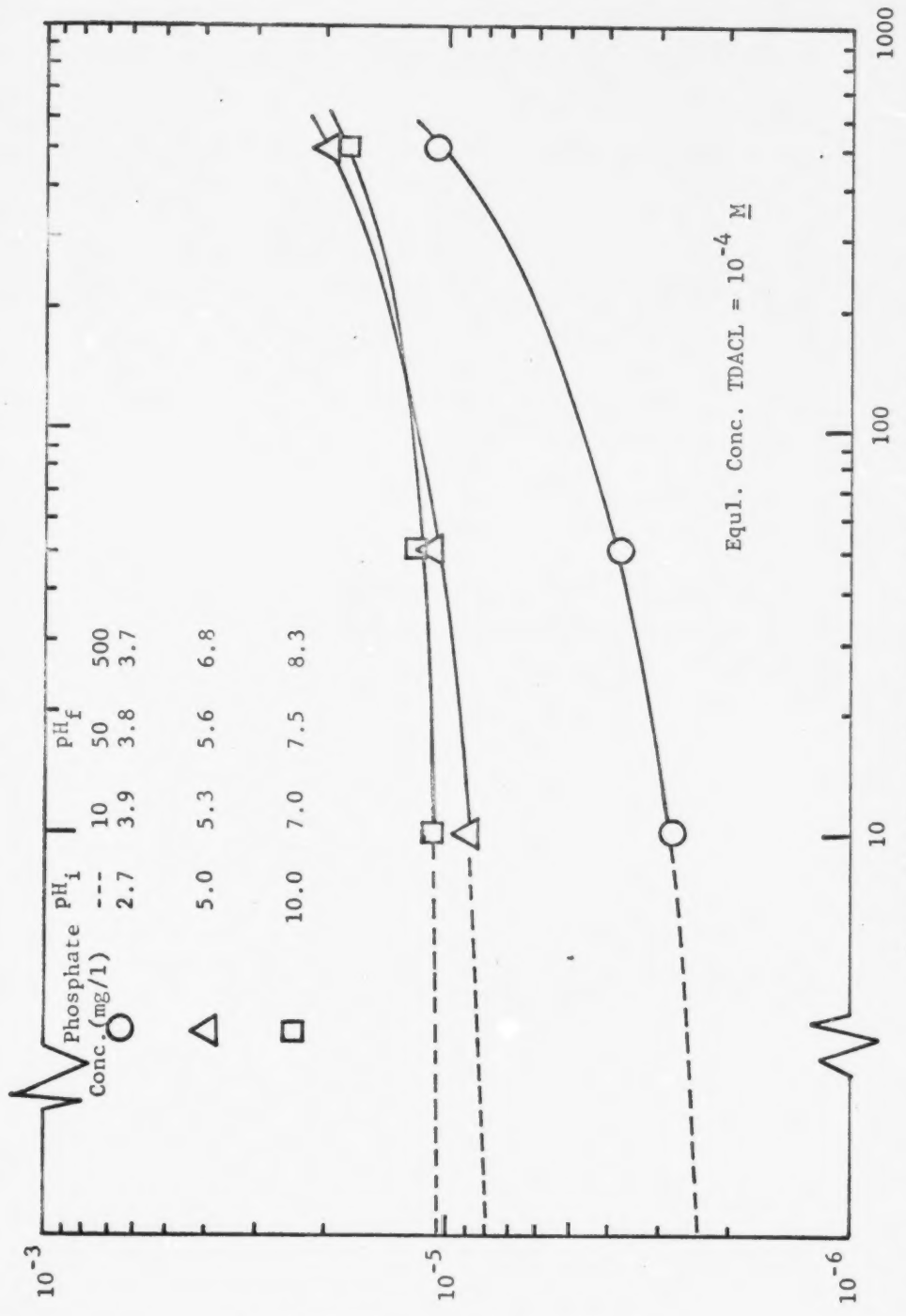

Figure 13.Effect of Sodium Hexametaphosphate on Adsorption of TDACL at 10^{-4} M TDACL

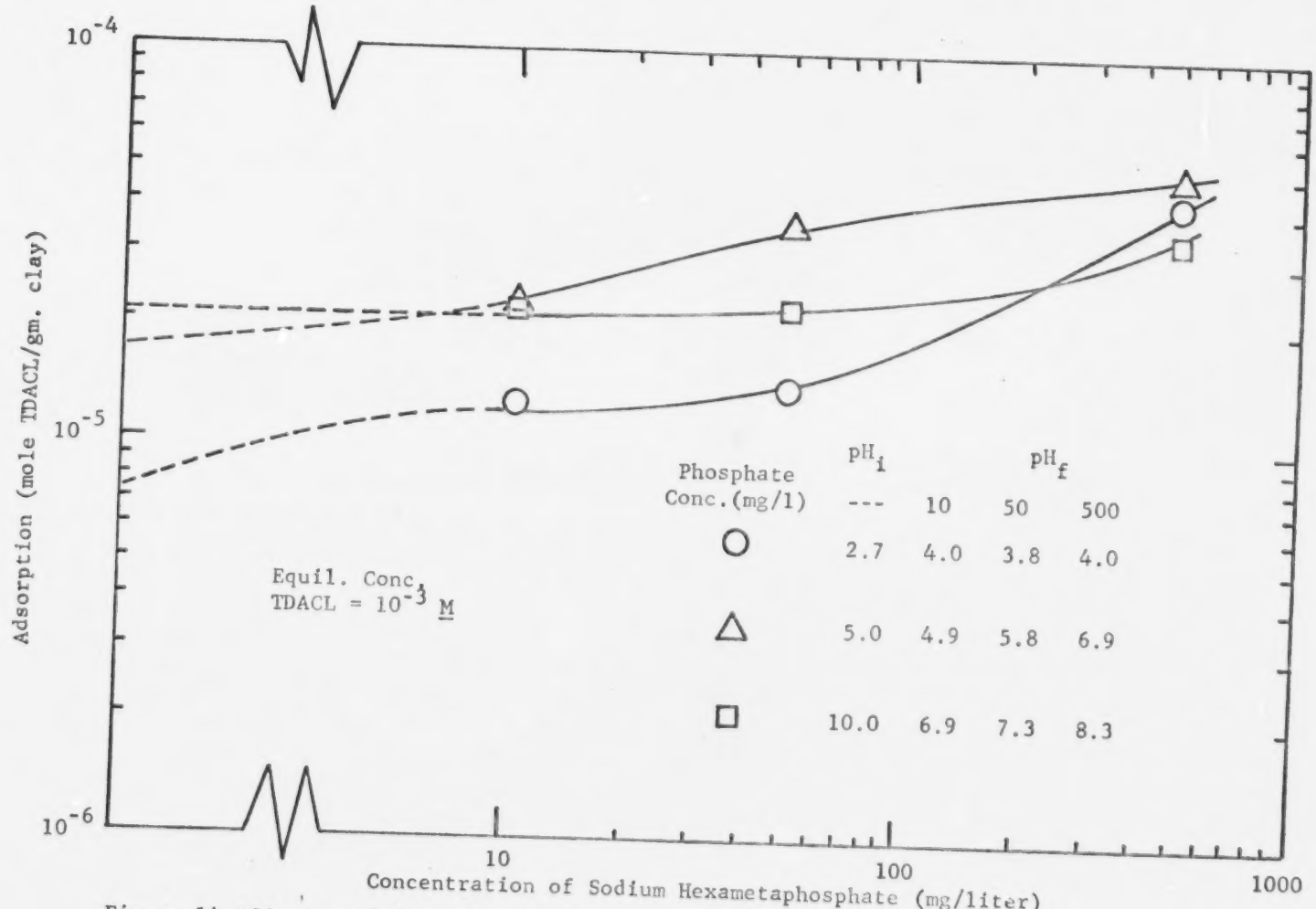

Figure 14. Effect of Sodium Hexametaphosphate on Adsorption of TDACL at 10^{-3} M TDACL

the phosphate increased adsorption of TDAC. Probably the phosphate both dispersed the clay creating more adsorption sites and by adsorption made the mineral more negative favoring adsorption of the cationic surfactant. The increase in pH_f with increasing phosphate concentration also should have aided TDAC adsorption as phosphate addition increased.

Streaming Potential Study of Kaolinite and Quartz

A number of studies have been made during the past decade of zeta potential of quartz in aqueous solution by the streaming potential method[9,11,12]. In addition, zeta potential of corundum in aqueous solution has been studied[13] by the streaming potential method. Much information concerning adsorptive properties and stability of colloidal suspensions of minerals can be obtained from such studies. For example, these investigations have indicated that the zero point of charge (ZPC) of quartz probably lies between pH 1.9 and pH 3.7 and that of corundum slightly above pH 9. For both minerals, since hydrogen and hydorxyl ions are potential determining[9,13], at pH values greater than the ZPC the minerals are negatively charged and at pH values less than the ZPC, positively charged. Thus, above the ZPC the minerals should tend to readily adsorb cations and below the ZPC, anions. Also, it has been noted by several authors that zeta potential can often be correlated with items such as adsorption density and contact angle[7,14,15].

In the present study zeta potential of quartz and kaolinite was measured in water as a function of pH. The quartz was studied in part to check proper operation of the streaming potential cell and to further study the variation of the ZPC of quartz according to various authors[9,11,12,16].

The streaming potential method appears particularly well suited for measurement of zeta potential of finely divided mineral particles. Streaming potentials may be measured by packing mineral particles in a glass plug

containing electrodes at both ends of the plug, forcing water (or other fluid) through the packed bed and observing, by means of an external circuit, difference of potential between the two electrodes. Streaming potential and zeta potential are related according to the following equation[17]:

$$\zeta = \frac{4 \pi \mu \lambda E}{DP}$$

where ζ = zeta potential

E = streaming potential

μ = viscosity of the fluid

D = dielectric constant of fluid

λ = specific conductance within the streaming potential cell

P = applied pressure difference

For this equation to hold true the flow of fluid through the plug must be laminar and the size of the pores between particles must be considerably larger than double layer thickness.

Methods and Materials

The quartz studied was the -48, +65 mesh fraction from a crushed and ground clear, colorless crystal of Brazilian quartz. The quartz sample to be studied was boiled for one-half hour in concentrated reagent grade HCl and then washed until the wash solution had a conductivity of less than 10^{-6} mhos/cm. Prepared quartz was then stored in low conductivity water.

The kaolinite used was the same material that was used in the other subprojects. It was prepared for use by hand crushing in a laboratory mortar and screening. The 48/65 mesh fraction was washed in low conductivity water and stored in plastic bottles until used. For streaming potential measurements the streaming potential cell was filled with material in such a way that the cell was completely filled with no voids between the

electrodes.

Water used was first distilled and then passed through a laboratory ion exchange column. Reagent grade HCl and NaOH were used to lower and raise pH of water used in the studies.

The streaming potential equipment and circuitry used was, in general, similar to that used by Gaudin and Fuerstenau[9]. An important difference included substitution of an EH Research Laboratories, Inc. Model 250 electrometer in place of the vibrating reed electrometer. Also a recorder was placed in the system much in the manner of Korpi[18]. The recorder made possible more accurate measurement of streaming potentials including some measurements where polarization or erratic behavior of the platinum electrodes was indicated but not sufficiently serious to preclude measurement.

Experimental Results

Figure 15 shows and compares zeta potential of quartz as a function of pH from the present work and from past studies[9,11,12]. In the present study it was not possible to measure streaming potentials below about pH 3 because of apparent polarization of the platinum electrodes used. However, an extrapolation of the curve from the current work shows quartz to have a ZPC of about pH 2.5. Concerning the other studies, bright platinum electrodes were used by Gaudin and Fuerstenau and by Li. Zucker used silver-silver chloride electrodes. The leveling off of the various curves at near neutral pH values except for the curve of Zucker, is probably due to surface conductance which may be a source of error in streaming potential studies where total ionic strength is less than 10^{-4} N[9]. However, the fact that Zucker's curve does not show the same leveling off in this range could indicate that the type of electrode used may influence results in this low ionic strength region.

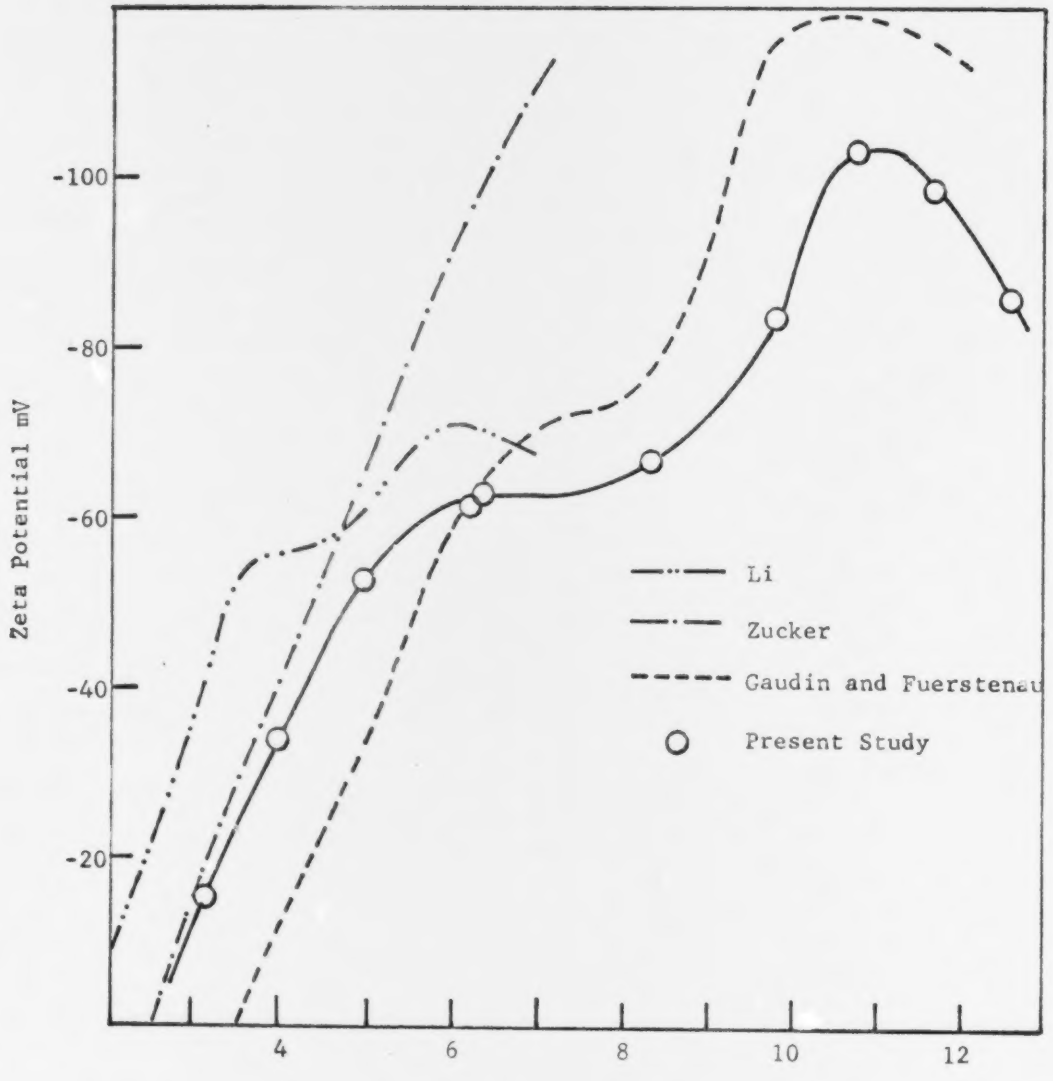

Figure 15. Zeta Potential of Quartz as a Function of pH by the Streaming Potential Method

The variation of ZPC of quartz according to different researchers has been noted before[16]. It should be noted that adsorption studies and microelectrophoresis studies generally place the ZPC near pH 2. It appears that past history of the quartz influences differences in ZPC. Greenberg, Chang and Jarnutowski[19] believe that the presence of small quantities of aluminum in solution may shift the ZPC toward more acid pH values. Also since silica is slightly soluble and quartz may well contain a surface layer of silica the quantity of silica in solution may well influence the ZPC. Thus, the surface area of the quartz in a streaming potential cell may influence ZPC as may also the solubility of the glass used in the cell.

Figure 16 shows and compares zeta potential of kaolinite as a function of pH from past studies[3,20,21] and from the present experimentation. All the older studies measured zeta potential by the microelectrophoresis method. Regarding these earlier experiments it is interesting to note that Bergna[20] used a plastic electrophoresis cell and that Street and Buchanan[21] and Iwasaki, et al.[3] used glass cells. The other data shown are from the present investigation. Note that some of these data are from streaming potential experiments and some are from microelectrophoresis experiments. Details of the microelectrophoresis technique are described in the next section of this report.

Two different investigators, N. Gjelsvik and Y. Narimatsu made the present streaming potential measurements. Curve #1 by Gjelsvik is now thought to be in error. In obtaining this particular curve thin porous silica discs were included in the streaming potential cell across the electrode. The procedure was followed to help contain the kaolinite and later was found to be unnecessary. Apparently, the streaming potential measured related more to the thin porous disc than to the kaolinite. Also for these measurements the

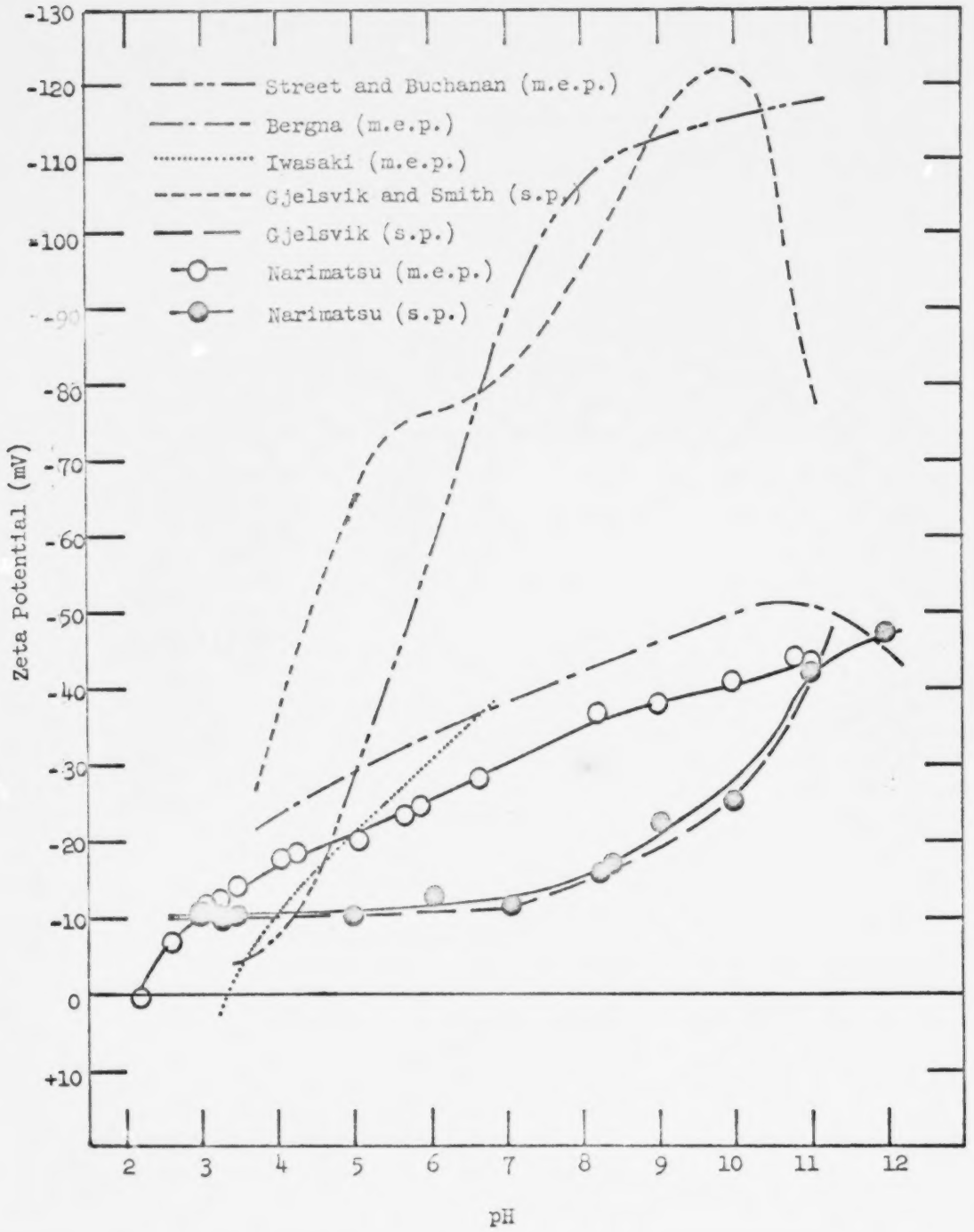

Figure 16. Zeta Potential of Kaolinite as a Function of pH

glassware was unaged. The other two curves from streaming potential technique (Gjelsvik # 2 and Narimatsu) are very close to one another and were run in well used and conditioned glassware. It should be kept in mind that streaming potential measurements at low ionic strength (less than 10^{-4} M) are probably in error because of surface conductance and the considerable thickness of the double layer under such conditions. Thus, near neutrality the zeta potential curves from the streaming potential technique are probably in error. This fact probably accounts for the differences between the curves from streaming potential (Gjelsvik # 2 and Narimatsu) and the curve of the present work from microelectrophoresis (Narimatsu). However, this phenomenon cannot account for the differences between the two curves at low pH values and for the fact that a ZPC is obtained for kaolinite from microelectrophoresis and not from streaming potential measurements.

Figure 17 shows zeta potential of quartz, corundum and kaolinite from streaming potential measurements as a function of pH. The quartz and kaolinite curves are from data of the current investigation. The corundum curve is from Modi and Fuerstenau[13]. It is interesting to note that over much of the pH range studied the curve for kaolinite is near an average value between those for quartz and corundum. Considering the chemical formulas for the three minerals, $Al_2(Si_2O_5)(OH)_4$, SiO_2 and Al_2O_3 respectively this fact is not surprising. It has long been known that quartz has a surface consisting of SiOH groups. A similar reasoning would suggest that the most probable surface for corundum would be one covered with Al-OH groups. At high pH and at low pH, however, the curve for kaolinite is below that of both quartz and corundum. At low pH this phenomenon could be explained on the basis of substitution of divalent ions for aluminum in the alumina (or "gibbsite") layer giving rise to a negative charge even at very low pH values.

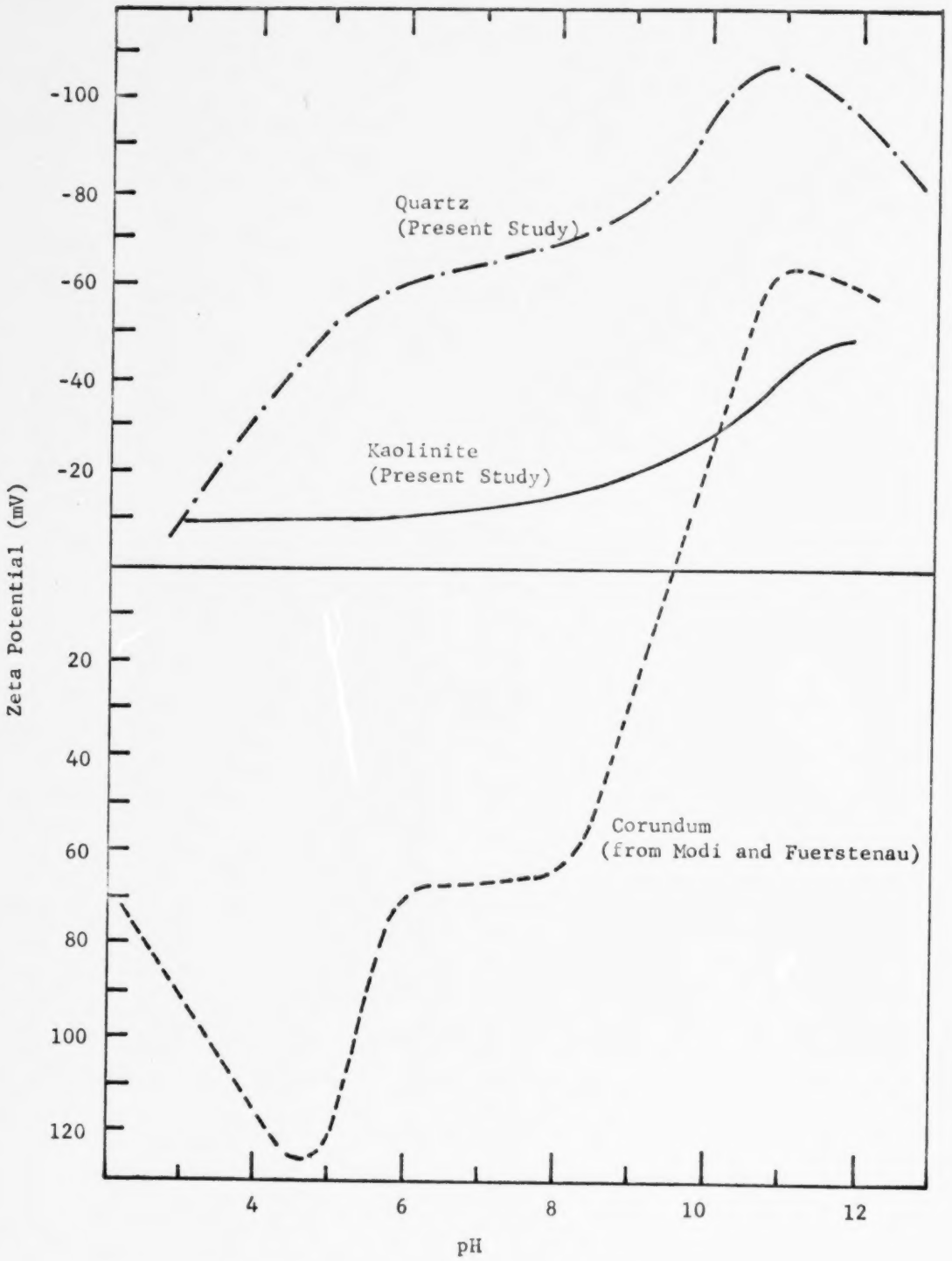

Figure 17. Zeta Potential as a Function of pH for Quartz, Kaolinite and Corundum by the Streaming Potential Method

Streaming Potential and Microelectrophoresis Study of Kaolinite Systems in the Presence of Alkyl Surfactants

All materials used in this subproject were the same as have been already described in sections on the other subprojects. The streaming potential measurements were performed in a manner that has already been described.

Microelectrophoresis experiments were carried out using a "zeta meter" manufactured by Zeta Meter, Inc., New York, N.Y. This apparatus consists of a power supply unit and control, a cell illuminator, a stereoscopic microscope and a plastic electrophoresis cell plus components such as platinum and manganese electrodes. Details of the apparatus are to be found in a brochure printed by the manufacturing company.

In the electrophoresis measurements the liquid as a whole is at rest in a cell while a particle such as a mineral particle in the cell moves through it under an external electric field in one direction along the potential gradient. Counter ions are attracted to the opposite direction by the electric field, which slightly lowers the velocity of the particle. In other words the ions in the immobile layer move with the particle while the ions in the diffuse layer, outside of the shear plane, move in the opposite direction to the particle. The effective viscosity in the diffuse layer is affected by the counter motion of the ions. This causes electrophoretic retardation. When the particle moves the double layer lags, which gives a relaxation effect on the particle. Regardless of these effects the velocity of the particle in a particular field is proportional to the zeta potential and to the external potential gradient. This relationship can be expressed as the following formula[17] (the Helmholtz-Smoluchowski formula):

$$\zeta = \frac{V}{E} \frac{4 \pi \mu}{D}$$

where ζ is the zeta potential; V is the electrophoretic velocity; E is the applied potential; μ is the viscosity of the bulk liquid; D is the dielectric constant of the bulk liquid.

Other formulae have been derived relating ζ to electrophoretic velocity, such as those of Huckel and Henry[17]. However, in the present study the Helmholtz-Smoluchowski formula was used for calculating zeta potential.

For microelectrophoresis measurements the kaolinite was ground as described earlier. Then the material was screened using a 100 mesh screen. Undersize material was placed in water for four hours so that the particles would become thoroughly wetted. Then the minus 5 micron material was separated from the rest by a settling method. The prepared minus 5 micron kaolinite particles were placed in low conductivity water under a CO_2 free atmosphere and stored for at least a week so that a proper electrical double layer would form.

Prior to making electrokinetic measurements a few drops of the relatively dense kaolinite were removed and diluted with low conductivity water to obtain the proper opacity necessary for measurement in the micro-electrophoresis cell. Then, a solution containing the reagent to be studied was mixed with this suspension toobtain the desired surfactant concentration. pH was adjusted by NaOH or HCl solution addition. The suspension thus prepared was vigorously stirred using a teflon stirring bar for five minutes under a CO_2 free nitrogen atmosphere.

For actual measurement the solution was placed in the electrophoresis cell and the electrodes properly positioned. The microscope was then set in such a way that the zero velocity layer was observed in the cell. This positioning was necessary because of movement of the liquid due to thermal overturn of the solution. The positioning was simple since the cell and

microscope were precalibrated.

The potential difference was applied and under the microscope the migration of a kaolinite particle was traced for a known distance, and its velocity was measured. The measurement of the velocity was repeated 10 times in each direction. After the electrokinetic measurement pH of the solution was again measured and this pH taken as the pH of the test.

Streaming Potential Results

Figure 18 shows zeta potential (ζ) of kaolinite as a function of sodium dodecylsulfate (SDS) concentration for various pH values as determined by the streaming potential method. The figure shows that in the acid pH range ζ of kaolinite tends to become increasingly negative with increasing SDS concentration. There is of course a dip in the curve for pH 3.0 possibly indicating an error in measuring ζ in the absence of a surfactant at pH 3.0. In the basic range ζ becomes more negative with increasing SDS addition until a particular SDS concentration is reached (about 10^{-5} M for pH 9.0 and about 10^{-6} M for pH 11.0). Above these particular SDS concentrations ζ tends to become less negative with further SDS addition.

The increasingly negative value of ζ in acidic solution can be attributed to the adsorption of dodecylsulfate ions (DS^-) onto aluminum sites (probably also onto silicon sites at the most acid pH values.) It is interesting to note that although the kaolinite is negatively charged it will adsorb negative DS^- anions and become more negatively charged. Of course there are undoubtedly positive charges on the kaolinite edges and adsorption of DS^- anions onto these sites should make the kaolinite more negative. But the magnitude of SDS adsorption onto kaolinite even when the kaolinite surface is negatively charged would seem to indicate that DS^- adsorption is taking place on other aluminum (and maybe silicon) sites

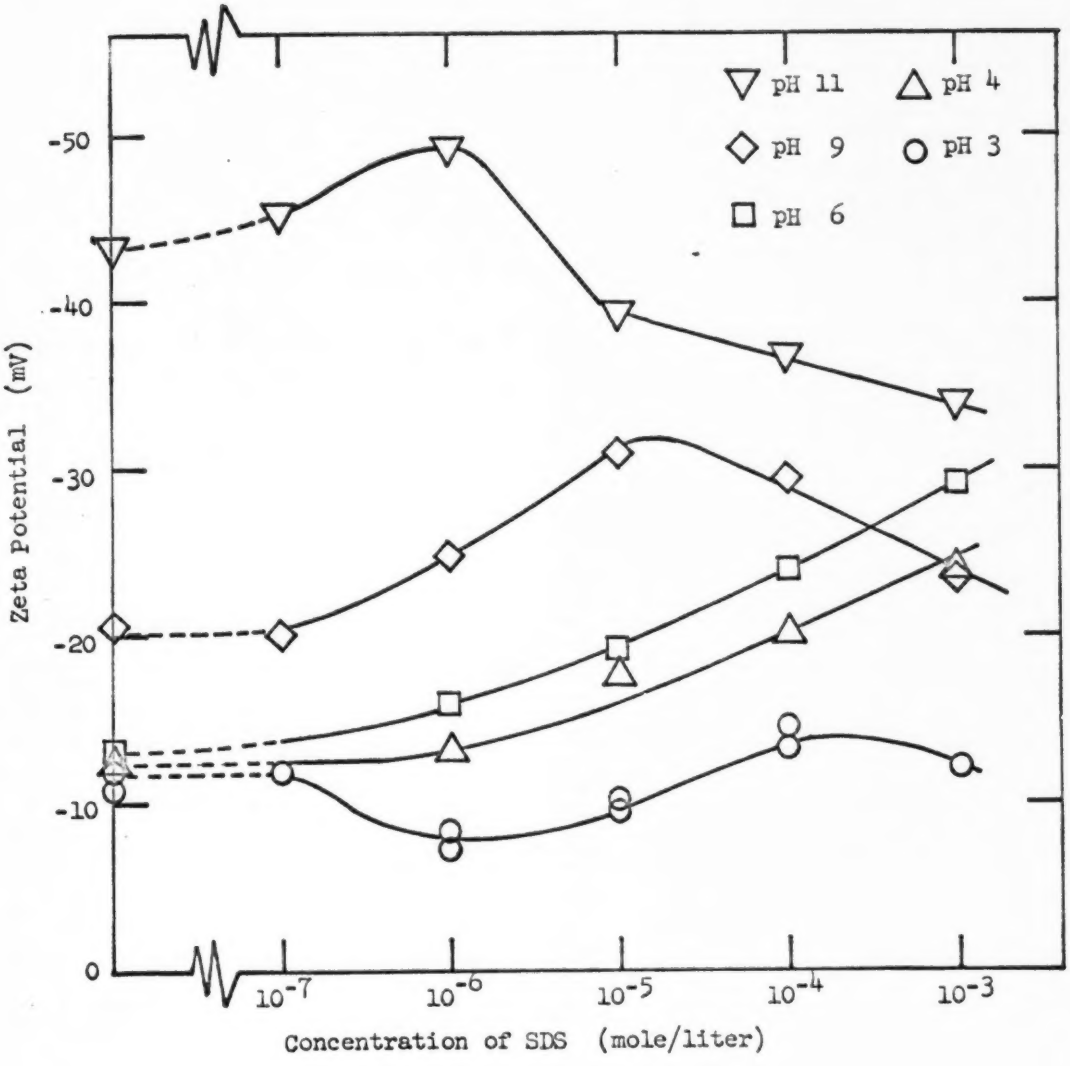

Figure 18. Zeta Potential of Kaolinite as a Function of SDS Concentration for Various pH Values by the Streaming Potential Method

in addition to edge sites. Thus, although the ZPC of kaolinite appears to be at a very low pH value the aluminum sites themselves seem to act as if they possessed a much higher ZPC as regards adsorption of DS^- anions. This result is consistent with the results of Figure 5 which indicated a ZPC of kaolinite from adsorption studies of around pH 4.

The decrease in negative value of ζ in the basic pH range with increasing concentrations of SDS at relatively high concentrations of SDS is probably caused by compression of the double layer due to the high ionic strengths present. There should be very little adsorption of DS^- anions in this region.

Figure 19 shows ζ of kaolinite as a function of trimethyldodecylammonium chloride concentration for various pH values as determined by the streaming potential method. In general the curves of this Figure tend to remain at a rather flat slope (or at acid to neutral pH values rises at very low concentrations of surfactant) until some surfactant strength is achieved (10^{-5} - 10^{-4} M). At greater surfactant concentrations than this critical concentration ζ becomes rapidly less negative with increasing TDACL concentration. In all cases the sign of ζ is ultimately reversed. This sudden drop in magnitude of ζ can be attributed to the so called himimicelle formation.

Figures 20 and 21 show respectively the effects of the presence of decyl alcohol (DA) on ζ of kaolinite in SDS and TDACL solutions. Note that in most cases the presence of decyl alcohol enhances the ability of the surfactants to change the magnitude of ζ. The effect is particularly marked in the acid range for SDS solutions. These findings are consistant with the adsorption data. Apparently decyl alcohol aids adsorption of surfactants by screening the repulsion between ionic surfactant leads. One effect of this would be to lower critical micelle concentration and presumably critical

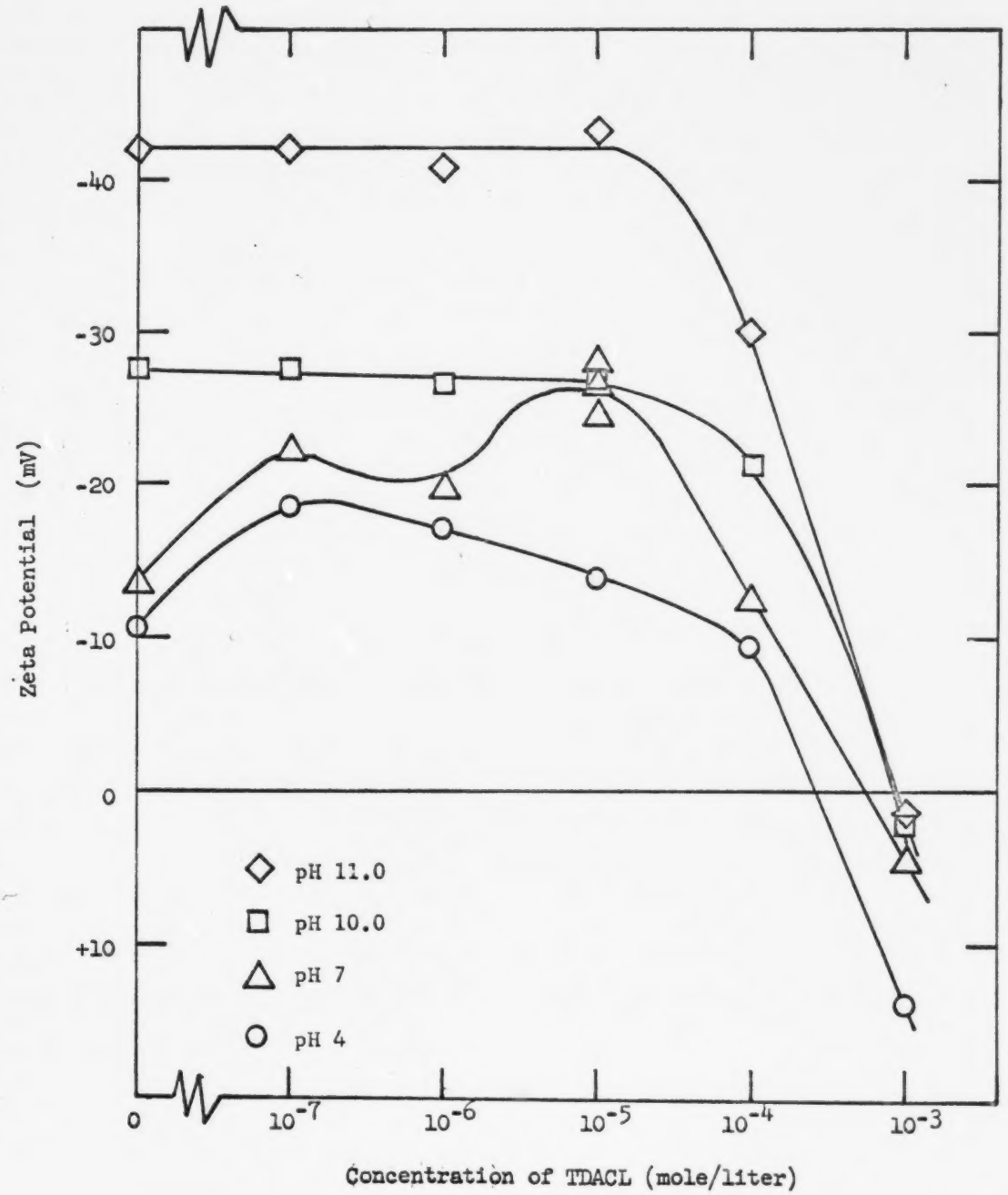

Figure 19.Zeta Potential of Kaolinite as a Function of TDACL Concentration for Various pH Values by the Streaming Potential Method

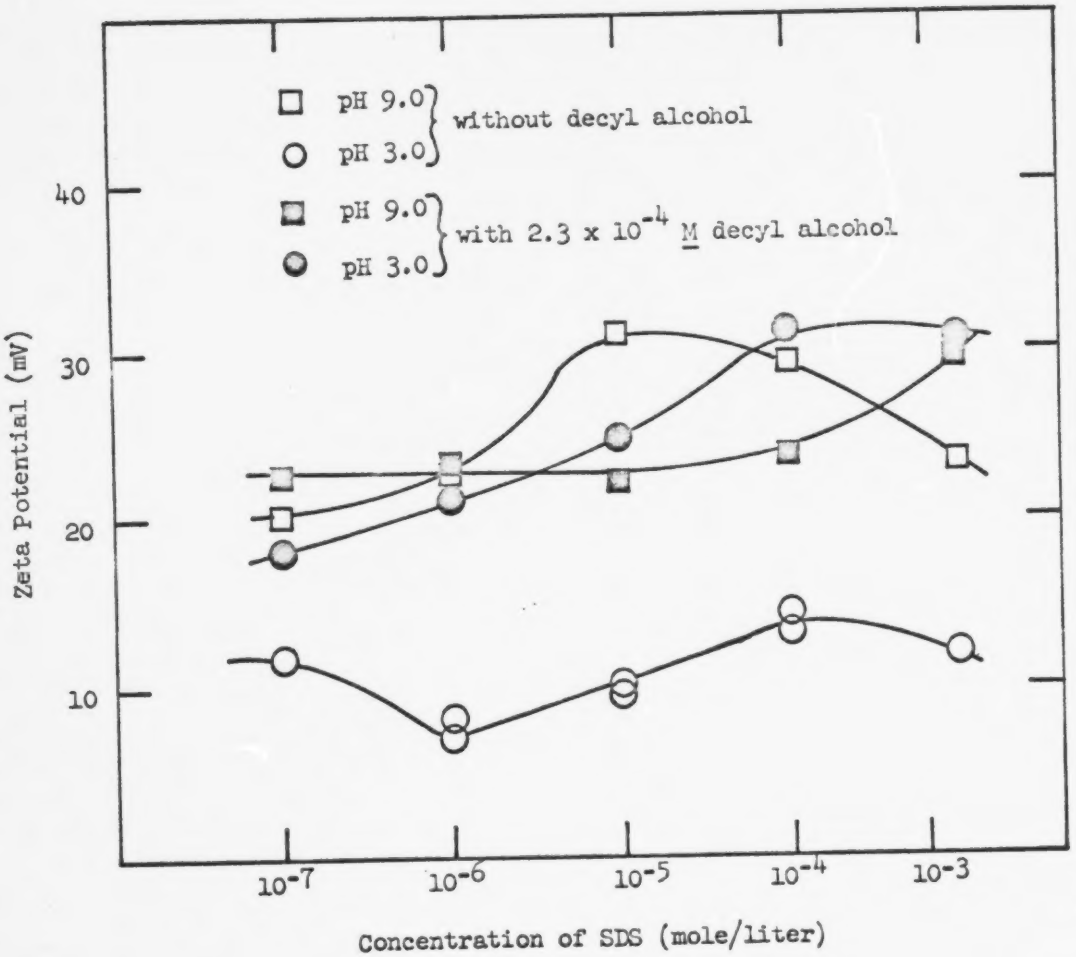

Figure 20. Zeta Potential of Kaolinite as a Function of SDS Concentration with and without the Presence of Decyl Alcohol, by the Streaming Potential Method

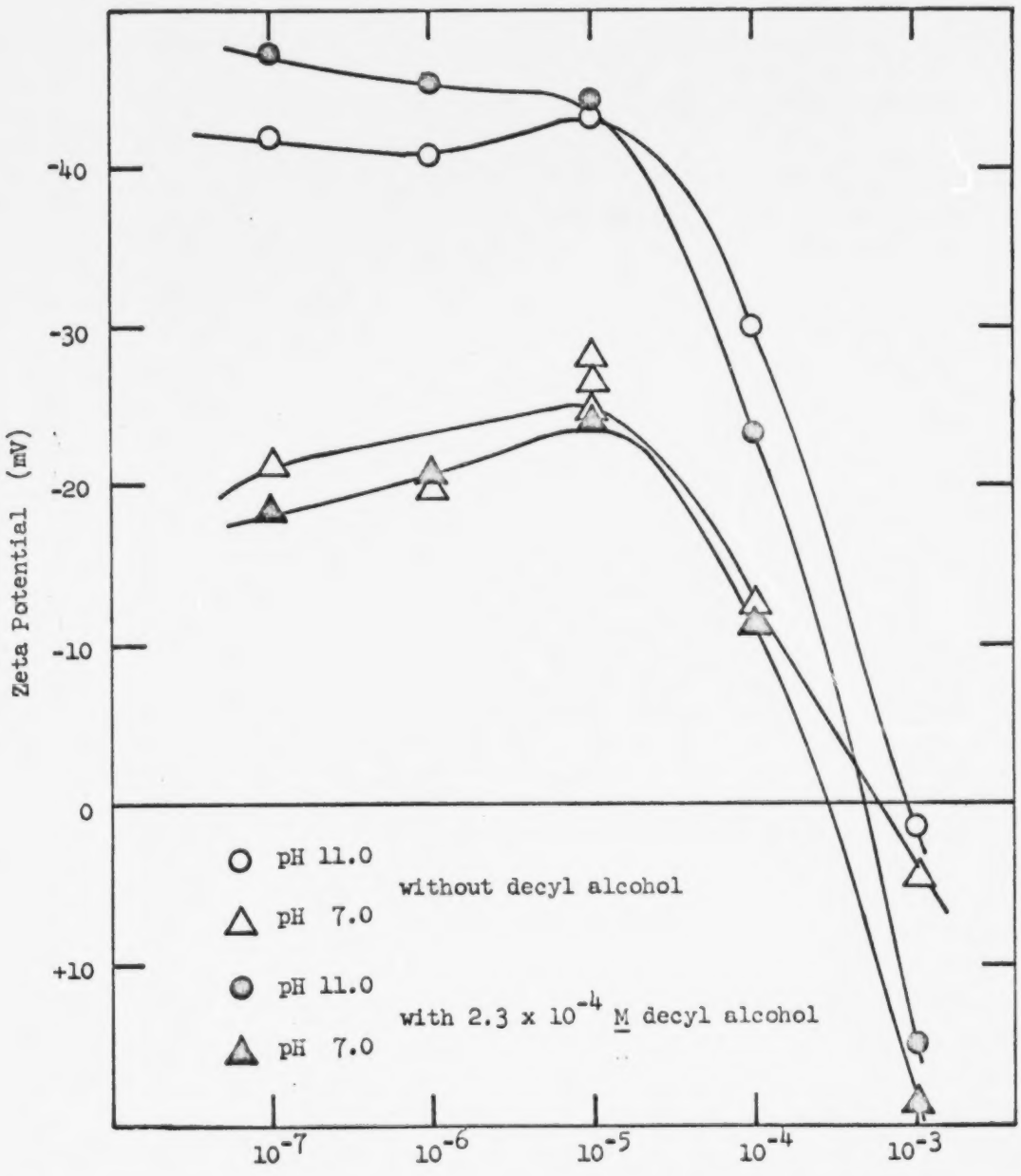

Figure 21. Zeta Potential of Kaolinite as a Funcetion of Concentration of TDACL with and without the Presence of Decyl Alcohol, by the Streaming Potential Method

hemimicelle concentration for a particular surfactant.

Figures 22 through 23 show data relating ζ to pH at various concentrations of the surfactants as determined by microelectrophoresis. These curves, of course, show substantially the same things as the curves from streaming potential measurements. The data from the two methods appear to be in qualitative agreement. Figures 24 and 25 make direct comparisons of the data from the two methods. The microelectrophoresis data are taken from the smooth line curves of Figures 22 and 23.

Infrared Study of the Adsorption of Alkyl Surfactants on Kaolinite

This portion of the study is somewhat incomplete because of the budget and time limitations of the grant. However, work will continue at the South Dakota School of Mines and Technology during the 1966-67 academic year on this particular subject under different funding.

Thus far, infrared patterns have been obtained for kaolinite treated with 10^{-2} M sodium dodecylsulfate and trimethyldodecylammonium chloride at pH 2.7, 3.4, 6.0, 9.0, 11.0 and 12.5. The technique used to obtain these patterns involved first placing 200 mg of kaolinite into 50 ml of 10^{-2} M surfactant solution and conditioning the sample with continuous agitation for either 2 hours or 36 hours. The two different conditioning times appeared to give the same results. pH was kept constant at a desired level by NaOH or HCl addition. After conditioning, the solids were allowed to settle. After the solids had settled, the upper 48 ml of solution was placed in a plastic bottle in which had been previously placed an Irtran window. The bottle was then placed in a centrifuge and a thin layer of kaolinite deposited on the Irtran window by centrifugation. Most of the liquid was then withdrawn from the bottle and the Irtran window and bottle dried at 65^{o}C for two hours. The prepared Irtran window was then used for obtaining the infrared spectra.

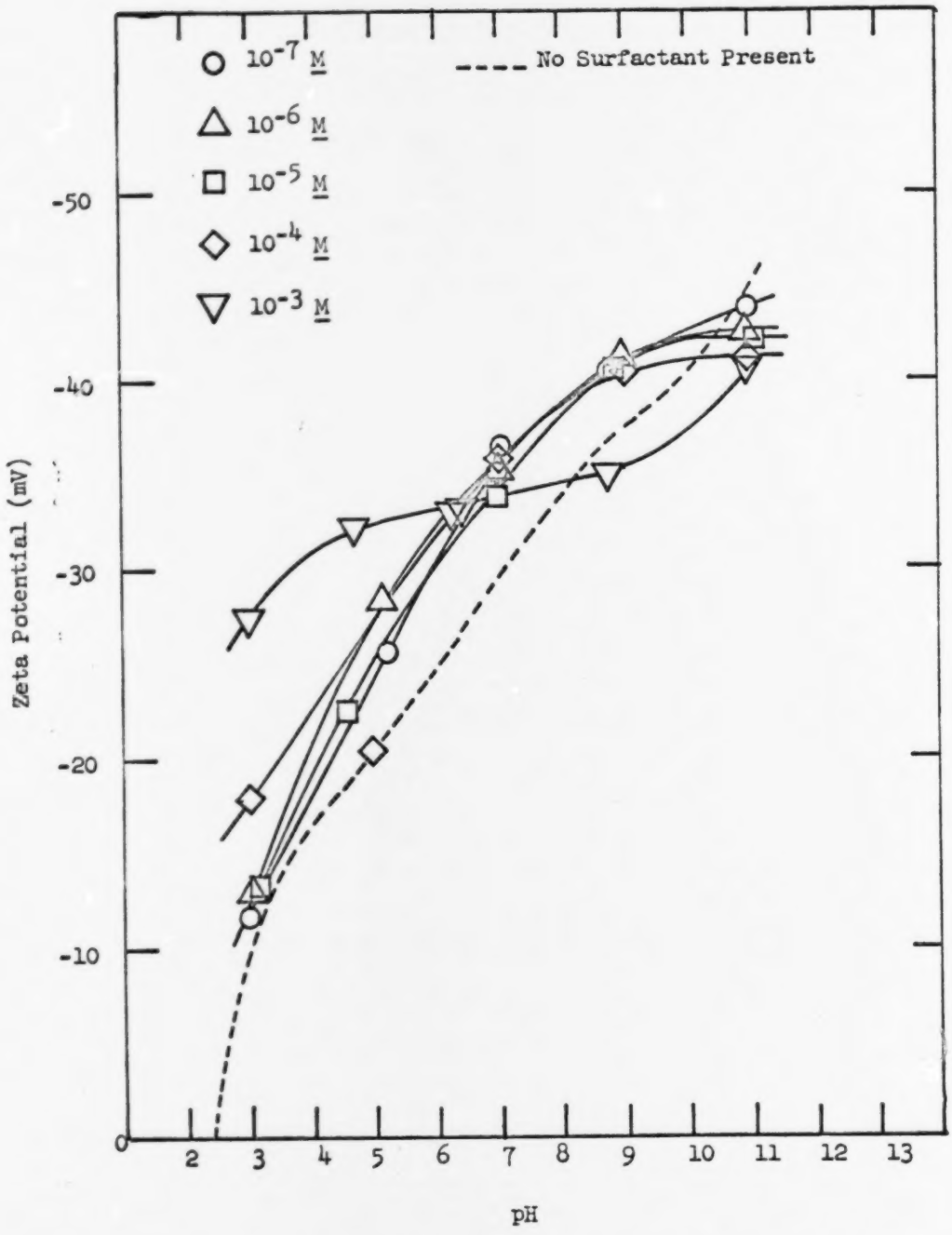

Figure 22. Zeta Potential of Kaolinite as a Function of pH for Various Concentrations of SDS - by Microelectrophoresis

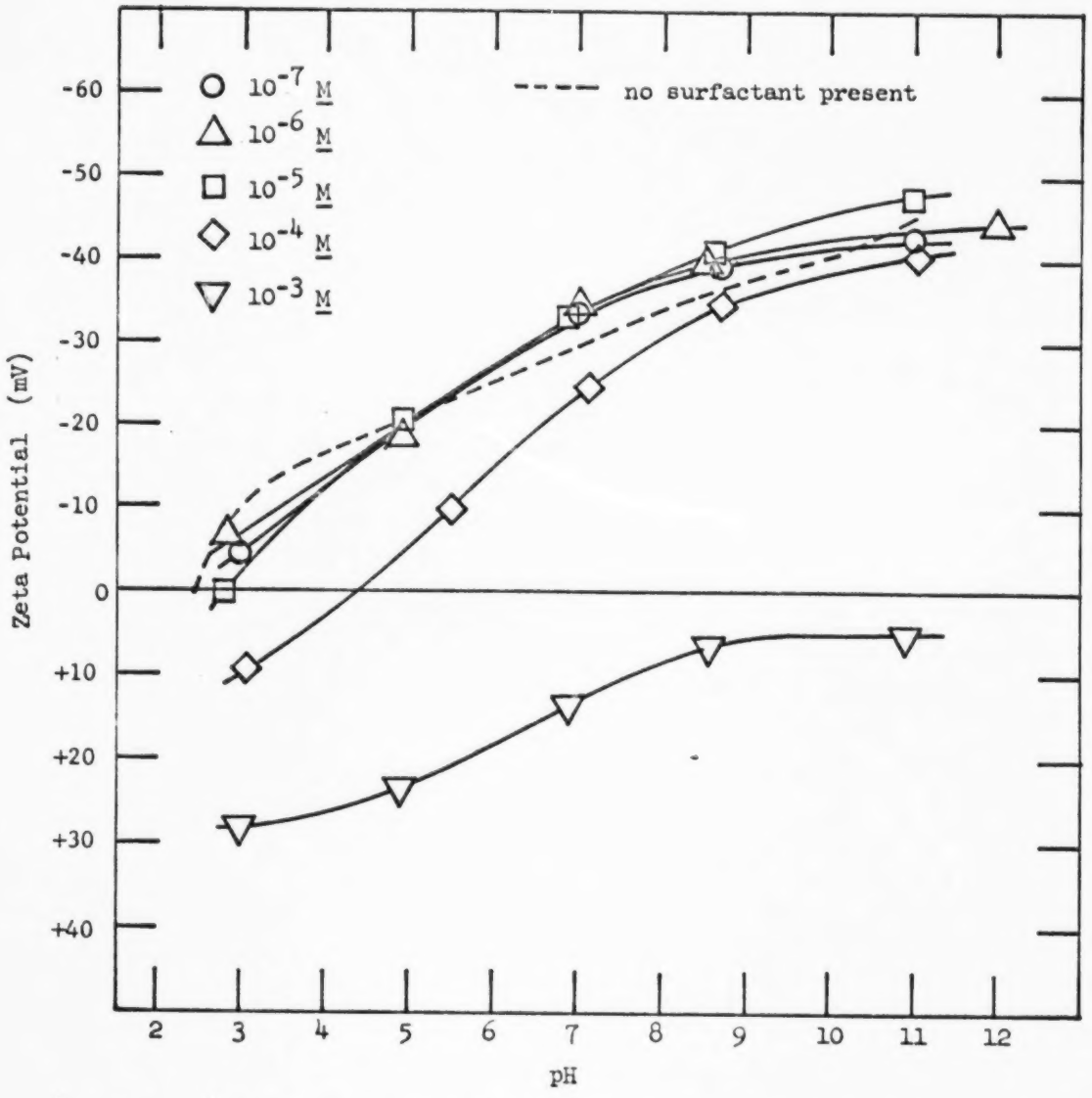

Figure 23. Zeta Potential of Kaolinite as a Function of pH for Various Concentrations of TDACL, by microelectrophoresis

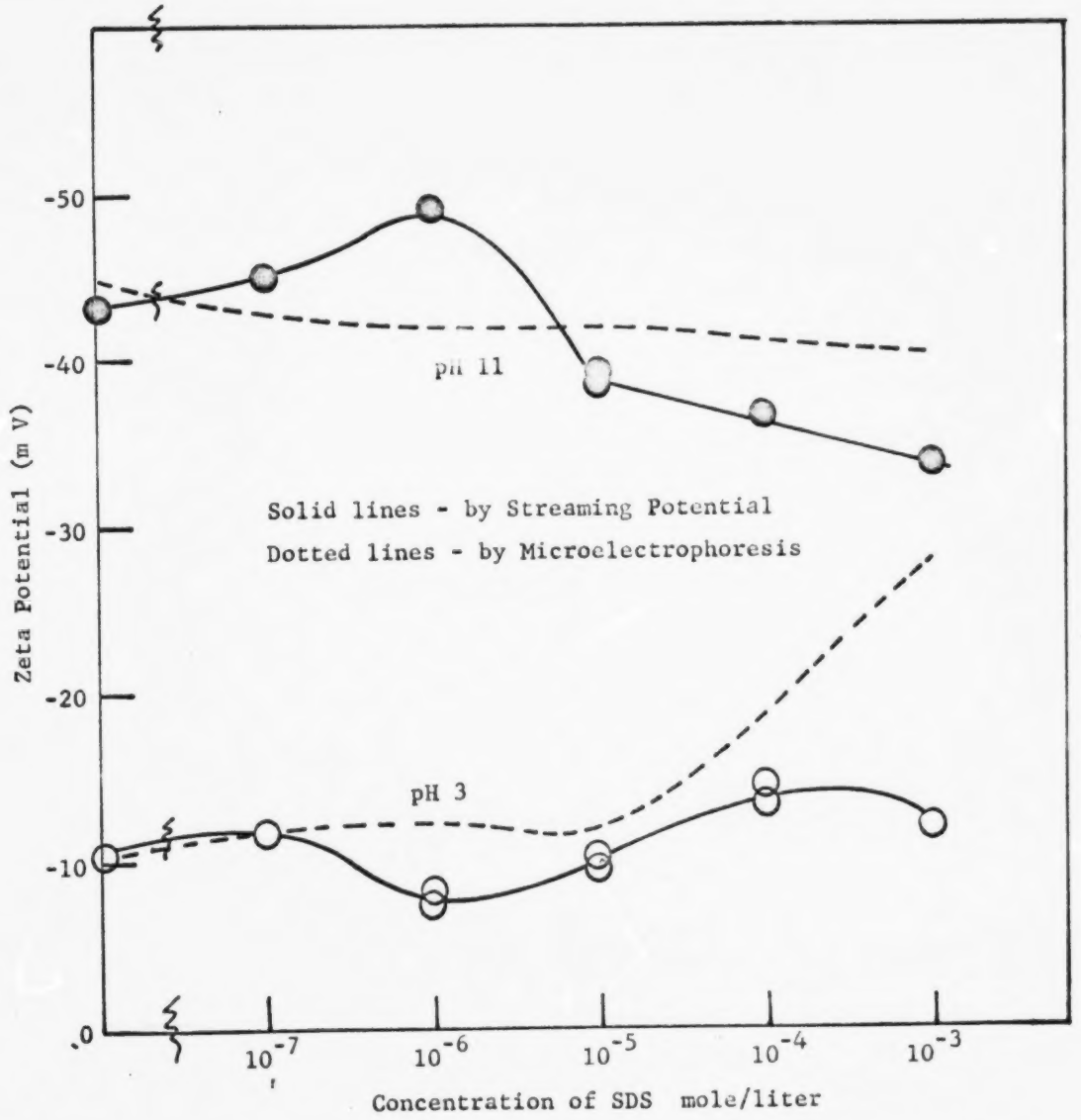

Figure 24. Comparison of ζ Data from the Streaming Potential and the Microelectrophoresis Techniques, Data for SDS Solutions.

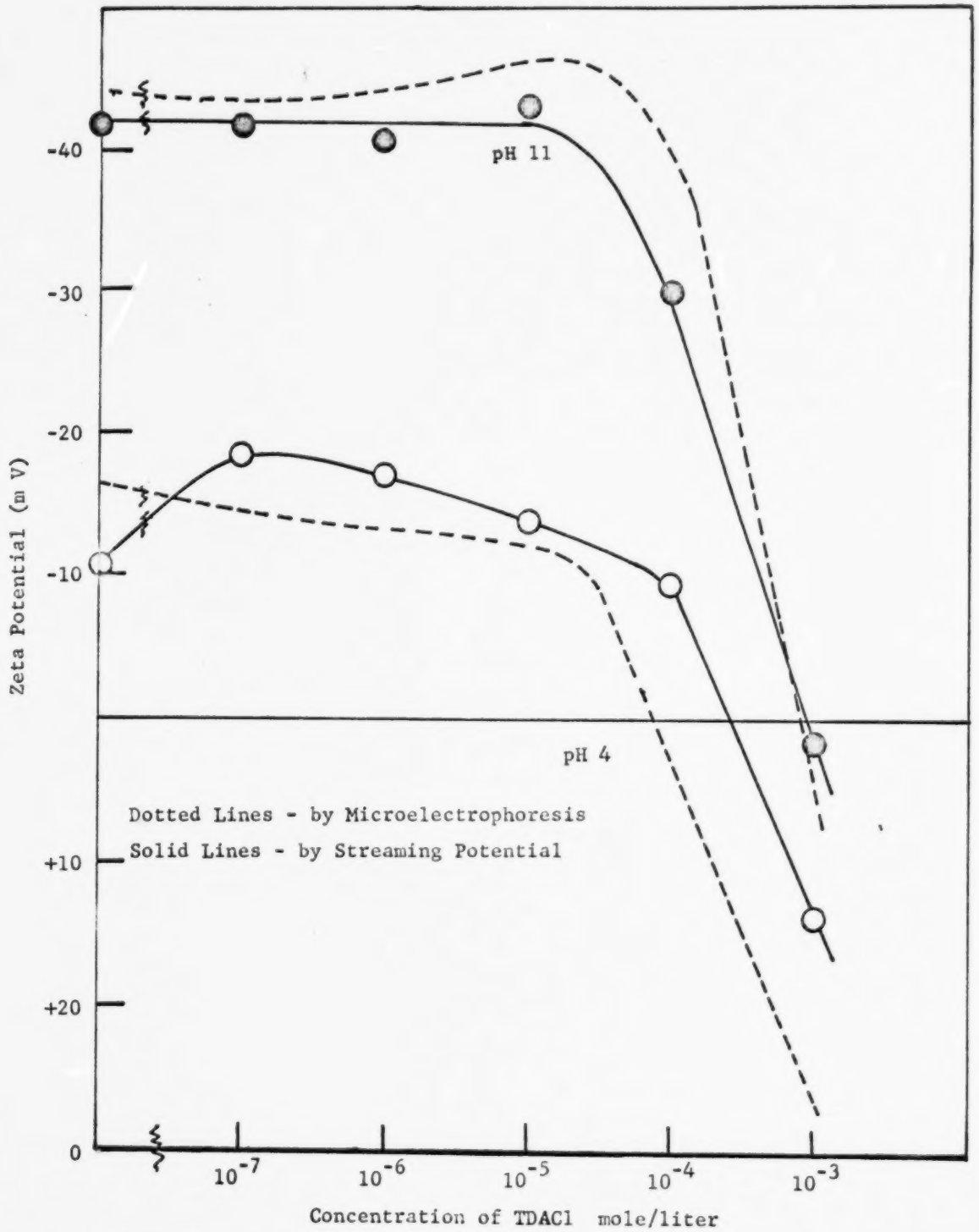

Figure 25. Comparison of ζ Data from the Streaming Potential and the Microelectrophoresis Techniques - For TDAC Solutions

Both sodium dodeylsulfate and trimethyldodecylammonium chloride were found to have been adsorbed. The CH_3 stretching frequency normally at 2930 cm^{-1} and the bending frequency normally at 1470 cm^{-1} appeared on the kaolinite patterns after treatment with the surfactants and were shifted to 2900 and 1460 cm^{-1} respectively. The drift was due to the kaolinite-sodium dodecylsulfate and the kaolinite-trimethyldodecylammonium chloride complexes formed. The bands were particularly strong at low pH value when adsorption of sodium dodecylsulfate was studied and at high pH values when adsorption of trimethyldodecylammonium chloride was studied. This indicated, of course, considerable adsorption of the anionic surfactant at low pH values and of the cationic surfactant at high pH values. It should be possible to develop this technique further to allow for the quantitative measurement of adsorption. Also it should be possible by the technique to study the effects of condensed phosphates and long chain alcohols on the adsorption of the ionic alkyl surfactants.

Contact Angle Study of the Effect of Surfactant Configuration on Adsorption of Surfactants

In this subproject the effects of ionization constant, solubility, and to a lesser extent hydrocarbon chain configuration on properties of a surfactant were studied. For this study only amines and quartz were used. The amines were selected for study because of their ready availability and quartz was studied because of its relative simplicity. The amines studied are tabulated in Table I which shows their source and approximate purity. Also shown are some physical constants relating to them. Some of the constants are from the literature and some are from measurements made during this project.

Several papers[7,14] have shown that often contact angle can be correlated with adsorption density and zeta potential. Furthermore, contact angles are

Table I
Properties of Various Amines

Amine	Source	Purity	Ionization Constant (K_b)	Solubility of Molecular Species (equiv./liter)	pK_a
Dodecylamine	Armour Industrial Chemical Company	triple distilled	4.3×10^{-4} (a)	2×10^{-5} (b)	10.65 (b)
N-methyldodecyl-amine	Lachat Chemical Company	+ 95%	10.2×10^{-4} (c)	1.2×10^{-5} (c)	11.01 (c)
1-methylundecyl-amine	Armour Industrial Chemical Company	unknown	4.3×10^{-4} (d)	2×10^{-5} (d)	10.65 (d)
di-n-hexylamine	Lachat Chemical Company	+ 99.5 %	10.2×10^{-4} (e)	appears to vary, could not be measured	11.01 (e)
dimethyldodecyl-amine	Lachat Chemical Company	+ 99.5 %	5.5×10^{-5} (c)	7.2×10^{-6} (c)	9.74 (c)
Trimethyldodecyl-ammonium chloride and hydroxide	Lachat Chemical Company	+ 99.5 %	~ 1 (the hydroxide is a very strong base)	not applicable	--

a) From Ralston[22], also measured in present investigation
b) From de Bruyn[23], also measured in present investigation
c) Measured in present investigation
d) Assumed to be close to values for dodecylamine
e) From Ralston[22]
f) From Sidgwick[24]

easy to measure. Thus, contact angle measurements frequently can be used as a convenient means of studying physical properties of surfactants as regards their adsorptive properties.

Experimental Procedure

Contact angles were measured in a conventional captive bubble contact angle device similar to the one described by Taggart, Taylor and Ince[25]. For the measurements several small, clear, colorless crystals of quartz were used. Several faces of these crystals were carefully polished using polishing wheels and successively finer aqueous suspensions of polishing alumina. The crystals were then carefully washed and stored in 1 N hydrochloric acid. Before each measurement the particular crystal to be used was carefully washed and tested in pure water for no contact. The crystals were frequently repolished. The reaction cell was lightly tapped before each measurement was made. The purities of chemicals used are shown in Table I. The pH was lowered by HCl addition and raised by NaOH addition except for the trimethyldodecylammonium hydroxide system where the amine itself was used to raise pH. In general a conditioning time of from 10 to 20 minutes was employed and conditioning was performed in the reaction cell.

Figure 26 shows contact angle as a function of pH for the dodecylammonium chloride system. Some of the 4×10^{-5} M data without alcohol addition are for dodecylammonium acetate. Most of the data of this figure are from earlier experimentation[7] and the figure is shown as a reference point. The figure shows curves for 4×10^{-5} and 4×10^{-4} M dodecylamine with and without dodecyl alcohol addition.

Considering the curves without alcohol addition it is thought that in the low pH region (up to about pH 6 - 7 considering the 4×10^{-4} M curve and up to pH 7 - 8 considering the 4×10^{-5} M curve) that amine ions adsorb as

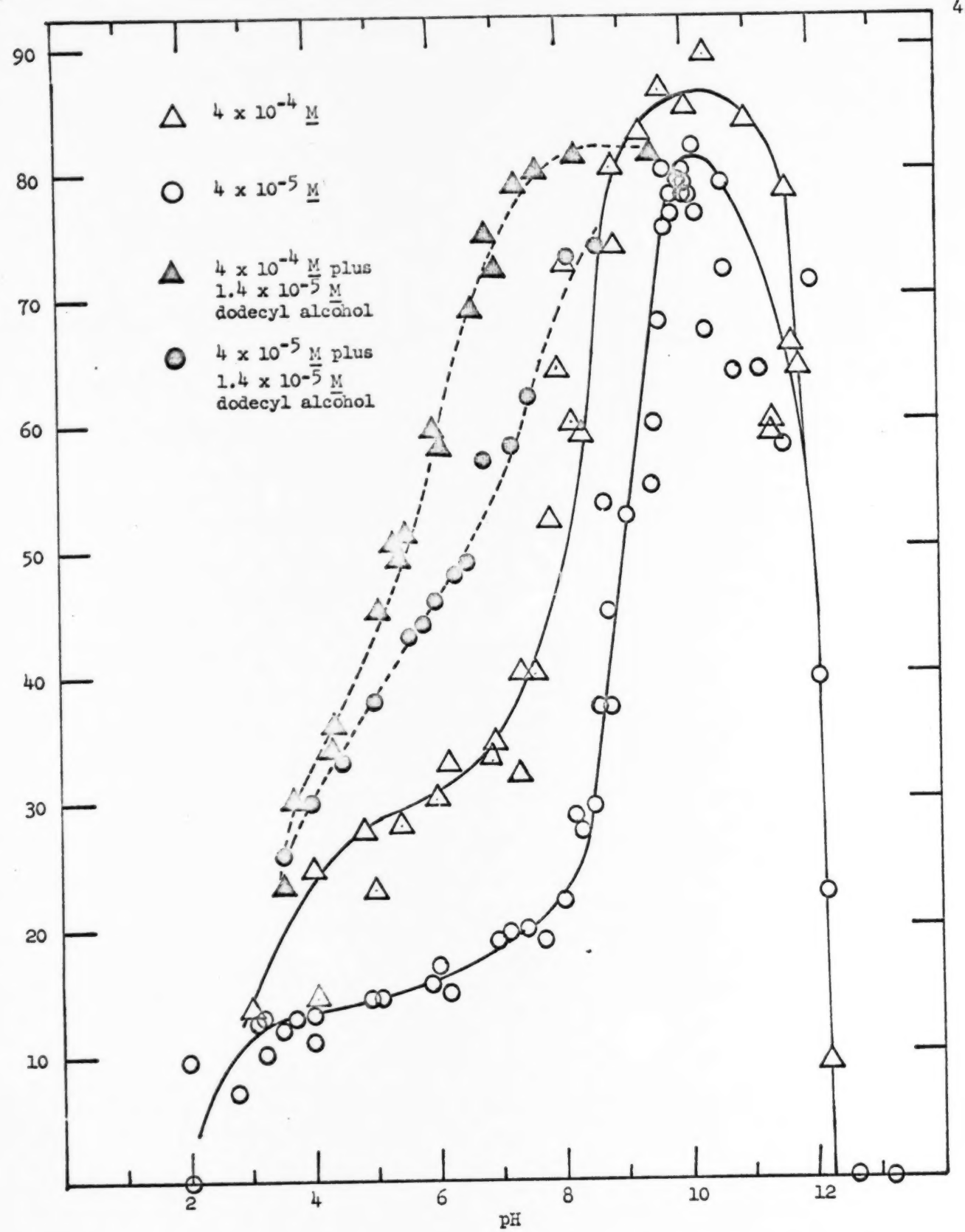

Figure 26. Contact Angle as a Function of pH for Quartz-Dodecylammonium Chloride Solution Systems

individual entities. These ions should adsorb wherever a negative surface site is present to neutralize the amine cation. At about pH 6 - 7 for the higher amine concentration and at about pH 7 - 8 for the lower, sufficient amine ions have become adsorbed at least within the diffuse part of the electrical double layer to exceed critical micelle concentration for the amine. There ions form highly charged "hemimicelles" which adsorb strongly onto the quartz. The reaction of course is pushed by the approximately 1 kT of energy that is associated with the expulsion of an equivalent of each CH_2 group from water[15]. Thus, as pH is increased above this point, adsorption, and consequently magnitude of contact angle, increases. Also because dodecylamine is a weak base($K_b = 4.3 \times 10^{-4}$) the "hemimicelles" should form more readily as pH is increased because of the ability of the molecular species of the amine to screen the charged heads of the amine ions. However, the fact that dodecylamine is a weak base coupled with the limited solubility of the molecular species (2×10^{-5} equiv/liter) ultimately places an upper pH limit on maximum amine adsorption. Thus, the drop off of magnitude of contact angle above pH 10 - 11 can partly be explained on the basis of increasingly fewer amine ions being available as pH is raised. Also it has been suggested that the Na^+ ions added with NaOH to raise pH compete with amine ions for surface sites at the higher pH values. That neutral dipoles coupled with alkyl cations tend to aid adsorption and therefore increase the magnitude of contact angle is confirmed by the results with the presence of dodecyl alcohol. It is to be noted that in the presence of dodecyl alcohol (a saturated solution or 1.4×10^{-5} M) the contact angle upswing with increasing pH starts at a lower pH value. Note, also, that all curves on this figure trend toward about pH 2 - 2.5 which is near the probable ZPC of quartz at about pH 2. This fact tends to point again to

the importance of amine ions in regard to adsorption of amine on quartz.

With this reference figure in mind it is interesting to observe similar figures for a secondary amine, a tertiary amine and a quarternary amine. Figure 27 shows contact angle as a function of pH for the n-methyldodecylammonium chloride solution systems. Figure 28 shows contact angle as a function of pH for the dimethyldodecylammonium chloride systems. Figure 29 shows contact angle as a function of pH for trimethyldodecylammonium chloride and hydroxide systems. The secondary unsymmetrical amine, N-methyldodecylamine, is a stronger base ($K_b = 10.2 \times 10^{-4}$) than the primary amine but at the same time is less soluble (1.2×10^{-5} equiv./liter). The tertiary amine, dimethyldodecylamine is a weaker base ($K_b = 5.5 \times 10^{-5}$) than dodecylamine and is also less soluble (7.2×10^{-6} equiv./liter).

The quaternary ammonium compound trimethyldodecylammonium hydroxide is of course an extremely strong base and is quite soluble in water.

Considering first Figure 27 for the secondary amine it is noticed that at relatively low pH values the curves for the secondary amine appear to be slightly to the left of the curves for the primary amine. The result is not unexpected for under these conditions amine ions should predominate and the secondary amine has the additional CH_3 groups which should enhance slightly both adsorption and magnitude of contact angle. At higher pH values the curves cross between pH 8 and 9 at an amine strength of 4×10^{-4} M and between pH 9 and 10 at 4×10^{-5} M. This phenomenon is also to be expected because of the lesser K_b value for the primary amine. Thus the primary amine starts hydrolyzing at a lower pH than the secondary amine. It should be noted, however, that a finite contact angle can be measured at no higher a pH in the secondary amine system than in the primary amine system.

Figure 28 for the tertiary amine shows additional evidence regarding the importance of hydrolysis in adsorption. Since dimethyldodecylamine is

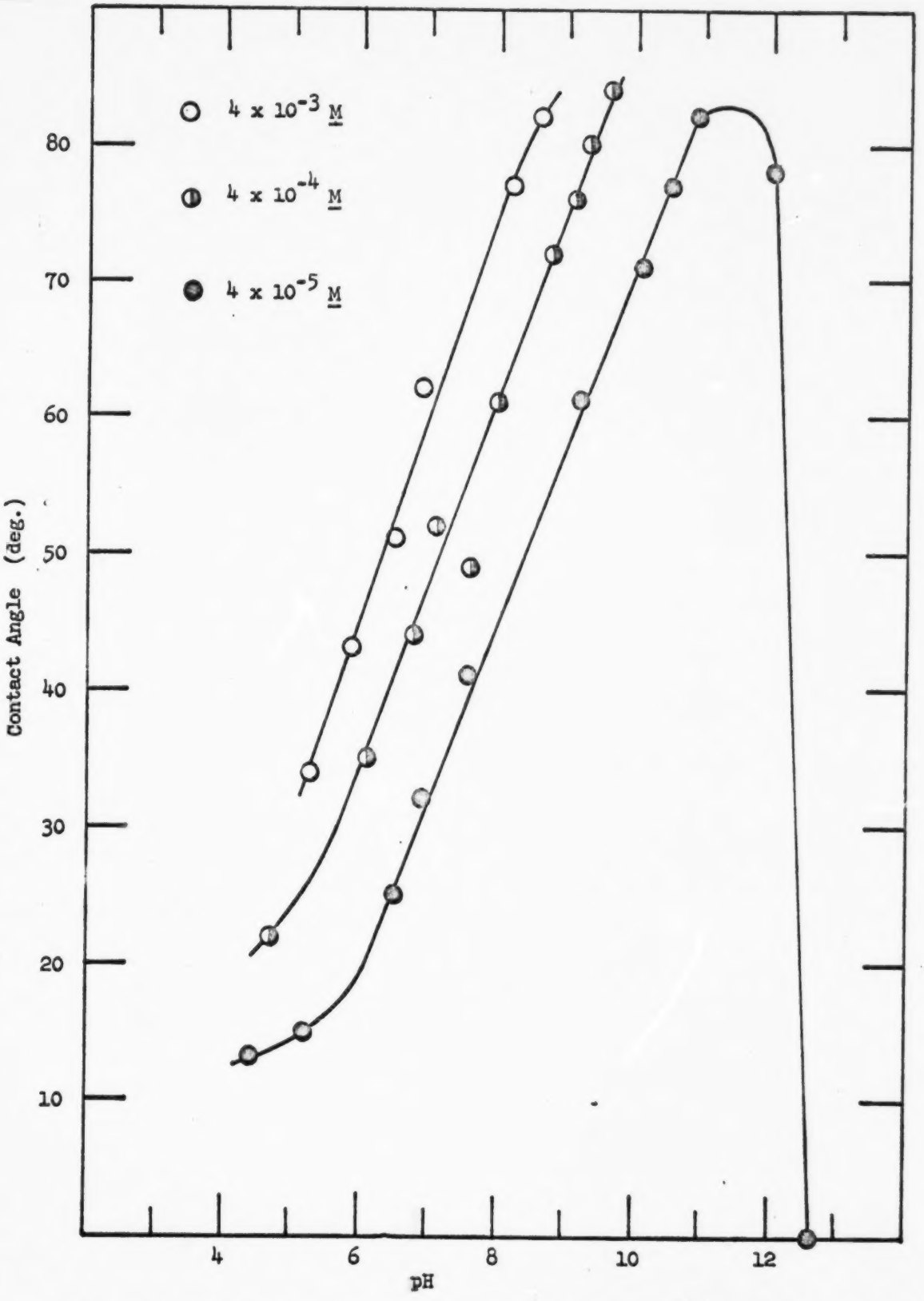

Figure 27. Contact Angle as a Function of pH for Quartz-N-methyldodecylammonium Chloride Solution Systems

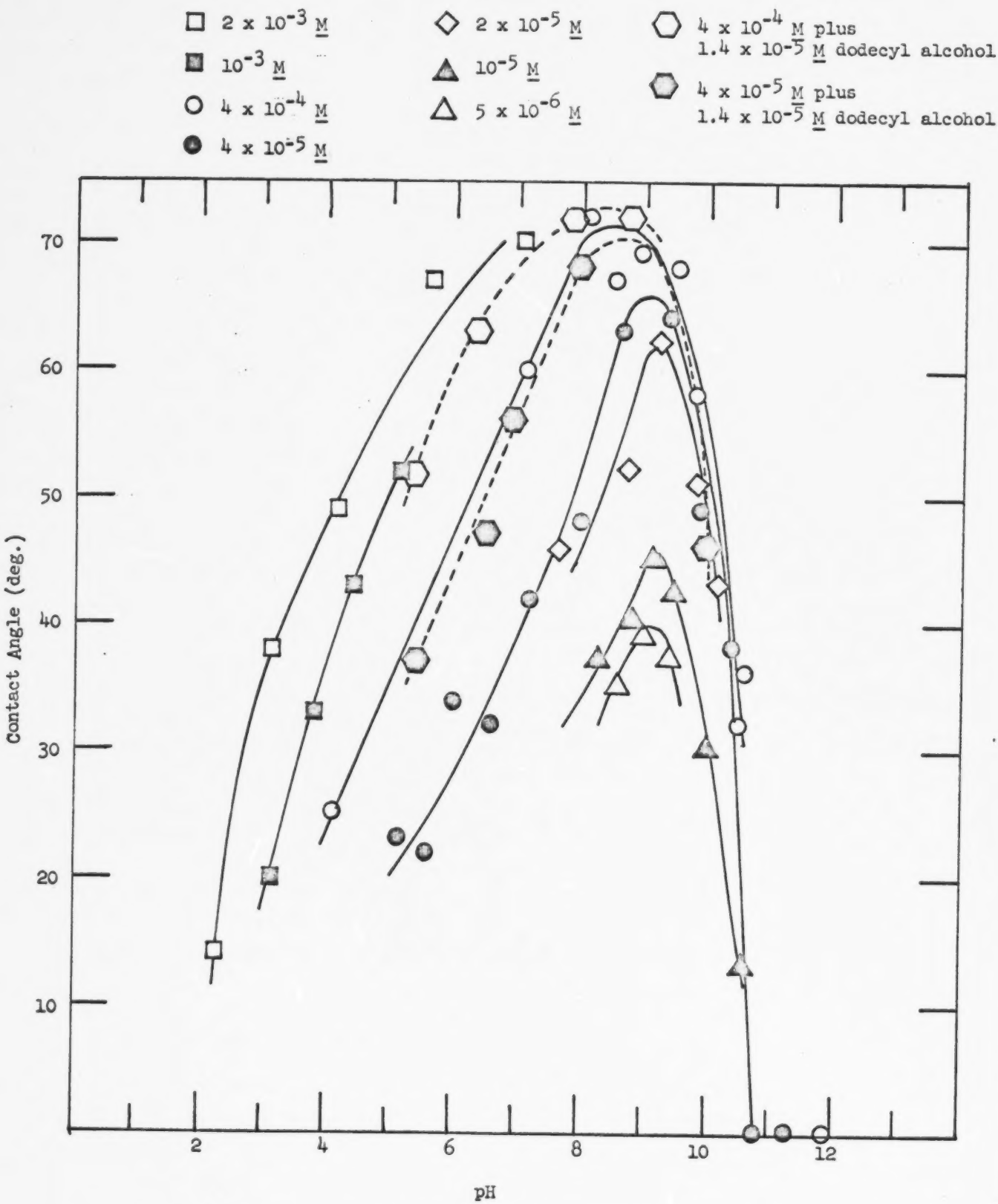

Figure 28.Contact Angle as a Function of pH for Quartz-Dodecyldimethylammonium Chloride Solution Systems

both a weaker base and less soluble than dodecylamine it is again not surprising that the pH of maximum contact angle (and presumably amine adsorption) is at a lower value than for the primary amine. The lower magnitude of maximum contact angle in this particular system probably results from the less negative original quartz surface at the lower pH of maximum contact angle (and optimum amine ion-molecule combination). Also contact ceases at a much lower pH. It should be noted, however, that the contact angle is generally slightly larger at lower pH values than for both the primary and secondary amines. This item probably reflects the presence of an additional CH_3 group over the secondary amine and two CH_3 groups over the primary amine.

Figure 29 for the quaternary ammonium compounds trimethyldodecylammonium chloride and hydroxide is extremely interesting. It shows that lack of amine ions at high pH, although important regarding the pH at which maximum contact angle is obtained, is not the only cause of ultimate cessation of contact. Furthermore, the curve for trimethyldodecylammonium hydroxide would seem to indicate that competition between Na^+ cations and amine ions is not an important factor relating to nil contact at high pH values. Thus, it would appear that the cessation of contact and adsorption may be related to the considerable solubility of quartz at high pH. Again it can be noted that an additional CH_3 group increases slightly magnitude of contact angle at low pH.

An item of interest regarding the four previous figures relates to the steepness of upswing of curves immediately above the pH at which sufficient ions and/or molecules populate the diffuse part of the double layer to cause hemi-micellization. The slopes for trimethyldodecylammonium chloride are much less steep than the slopes of curves for the other amines. The observation is reasonable, for, as pH is increased above this point in the systems containing amines that hydrolyze, not only is there an increasing tendency

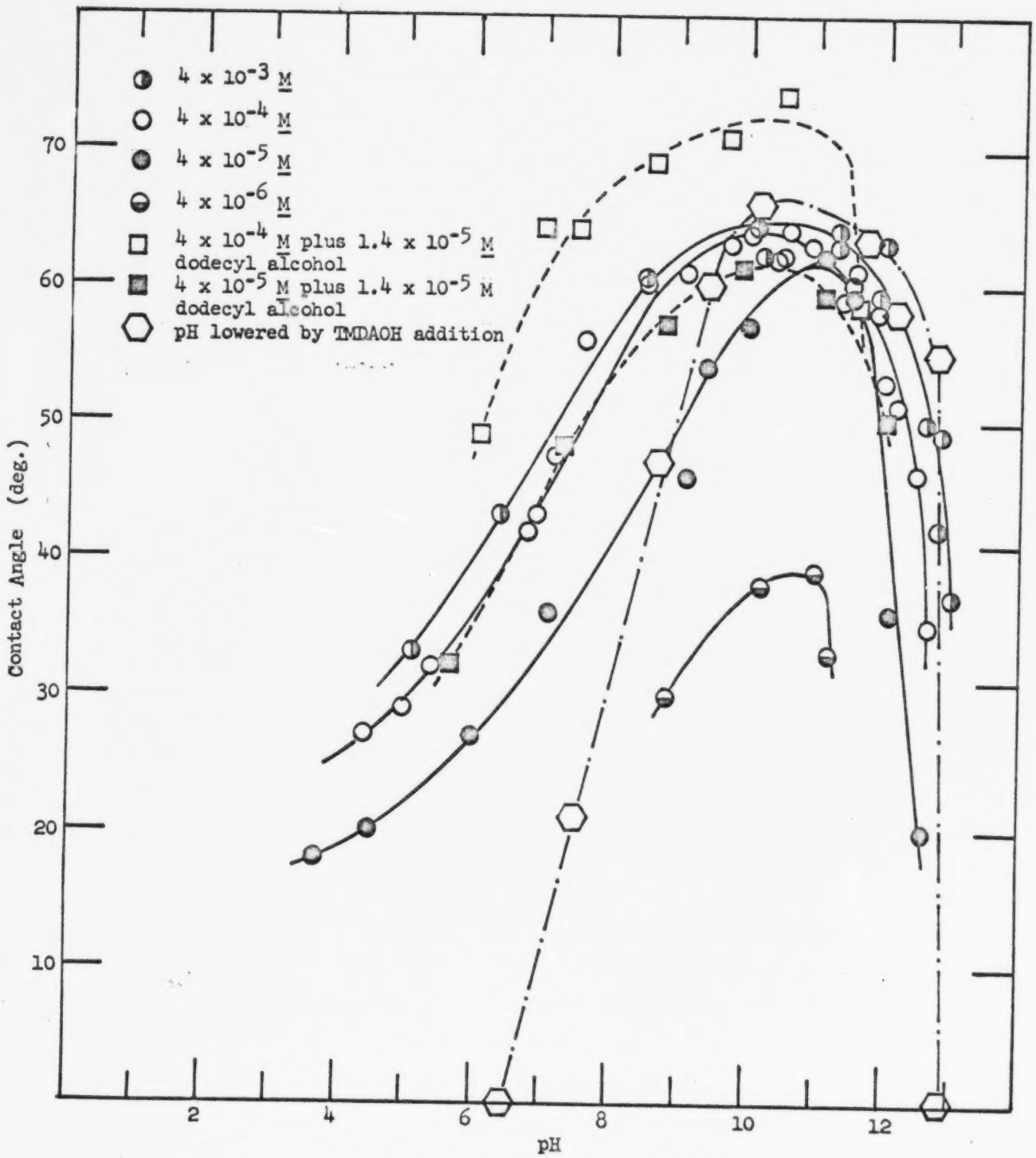

Figure 29. Contact Angle as a Function of pH for Quartz-trimethyldodecylammonium Chloride and Hydroxide Solution Systems

toward hemi-micellization because of an increasing population of ions within the double layer but also the molecular species becomes increasingly more numerous. Thus, as pH is raised in these three systems charged ionic heads are increasingly screened and critical hemimicelle concentration is lowered. Therefore, the upswing curve should be steeper.

Figures 30 and 31 show respectively contact angle versus pH curves for di-n-hexylammonium chloride (a symmetrical secondary amine) and for 1-methylundecylammonium chloride. These substances were studied to learn a little of the effect of hydrocarbon chain configuration on adsorptive properties of amines (and indirectly surfactants in general). Obviously the magnitudes of contact angles obtained for a particular amine concentration in the di-n-hexylamine systems are smaller than in the other systems studied. Apparently the breaking up of the hydrocarbon chain into two chains of equal length considerably reduces its effectiveness. It would be interesting in the future to also study a twelve carbon amine with a double bond in the middle of the chain for comparison purposes. Also of interest concerning the symmetrical secondary amine was the strange solubility behavior of the molecular species of the amine which seemed to depend on pH. The ionization constant (10.2×10^{-4}) as determined by Ralston[22] was assumed to be correct.

The figure for 1-methylundecylammonium chloride shows this substance to behave quite similarly to linear dodecylammonium chloride. For reference a curve for dodecylammonium chloride at the same amine strength is also shown on the figure.

Stable and Dynamic Contact Angles

It was found in several of the amine systems in which the amine hydrolyzed that contact angles at relatively high pH values and amine concentrations were

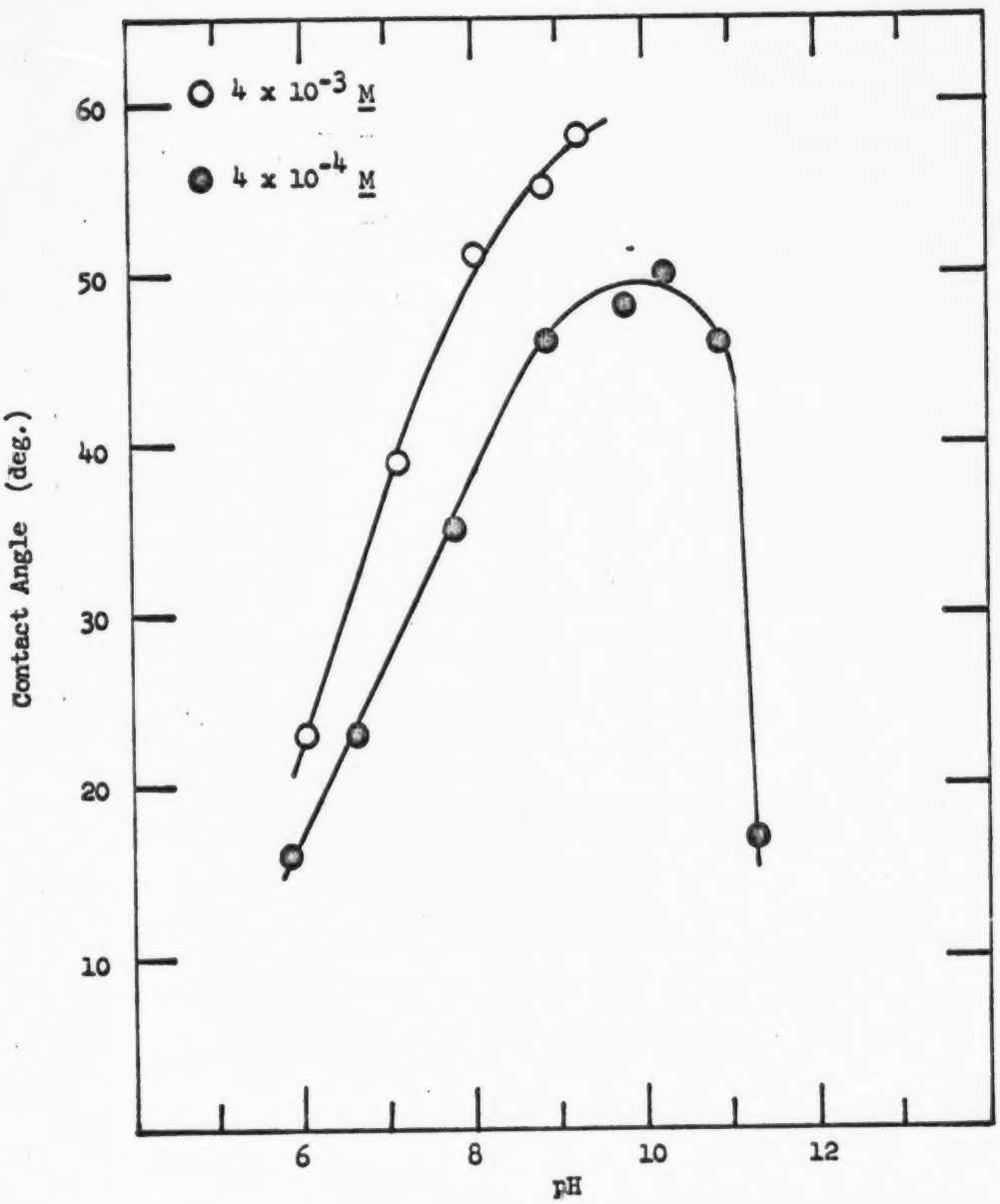

Figure 30. Contact Angle as a Function of pH for Quartz-dihexylammonium Chloride Solution Systems

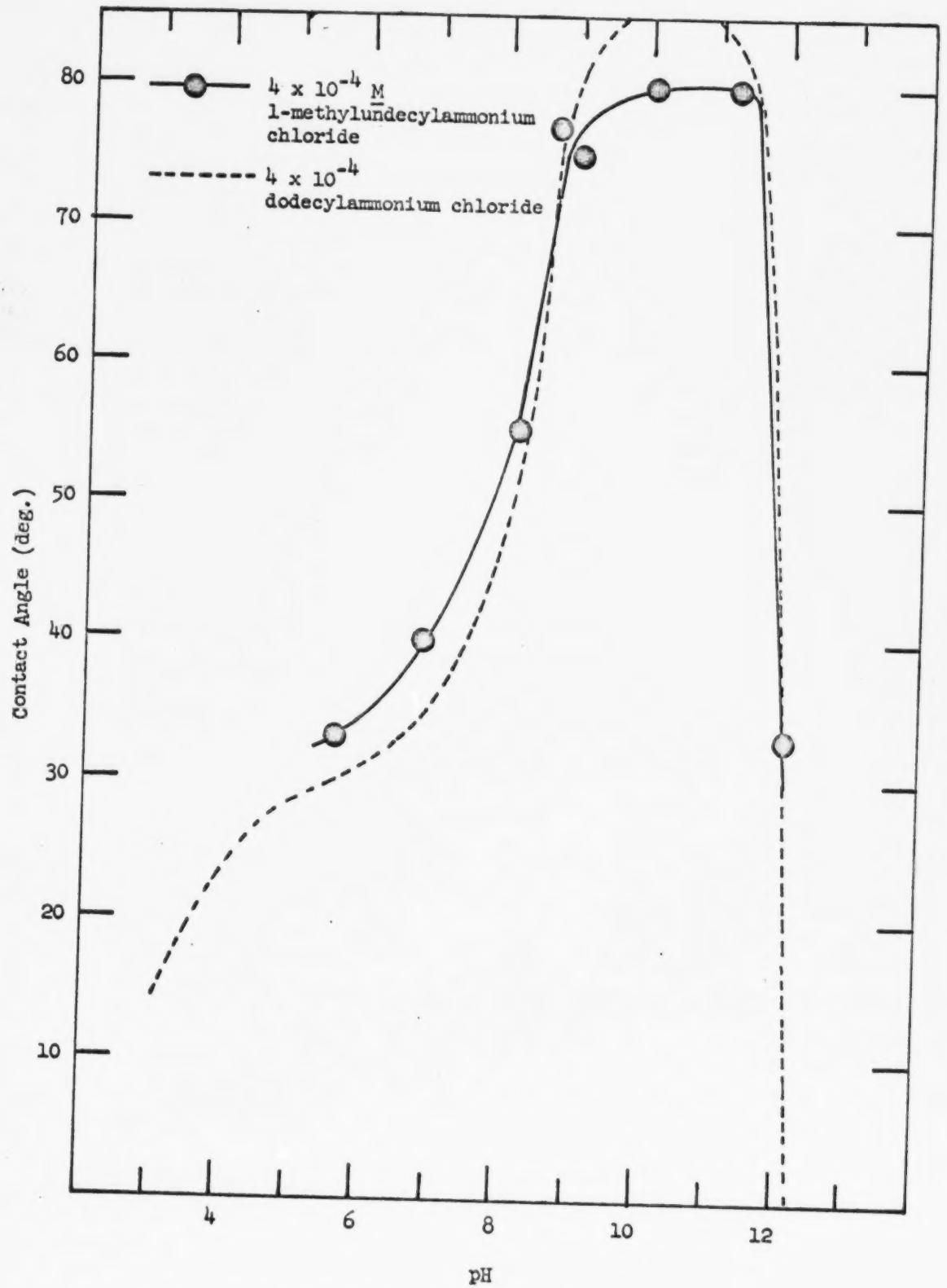

Figure 31. Contact Angle as a Function of pH in Quartz-1-methylundecylammonium Chloride Solution Systems

unstable. Thus, all angles reported in the previous figures are "stable" angles up to some pH values above which they are the largest angles that could be measured in the systems after bringing a fresh bubble in contact with the conditioned mineral surface. Details regarding the angles will be given in a paper soon to be published[26].

Figure 32 shows how these maximum "dynamic" angles compare with stable angles that ultimately could be obtained in the same system. The amine concentration was 4×10^{-4} M. Also shown in the figure are "measured in water" angles. For the measurement of these angles the quartz crystal was first conditioned for the normal time in surfactant solution at a particular pH value. The crystal was removed from the surfactant solution and placed in water of the same pH as the surfactant solution. The contact angle was then measured in water.

The phenomenon of contact angles that decrease in magnitude as a function of time have been attributed to the presence of precipitated amine molecules (the phenomenon does not occur in the quaternary amine system). Furthermore, while these angles change in magnitude there appear to be changes in both interfacial tension solid-air and interfacial tension liquid-air.

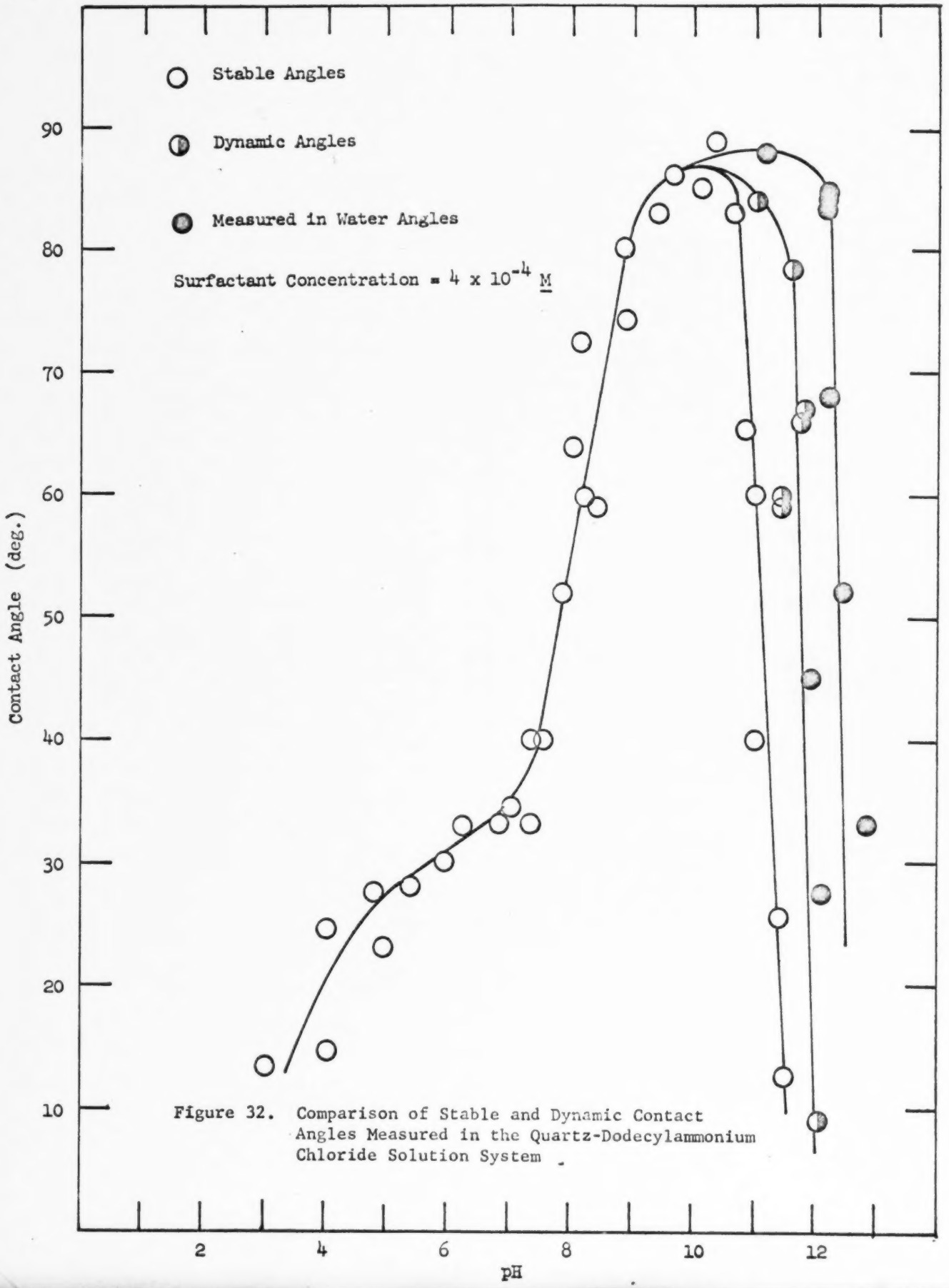

Figure 32. Comparison of Stable and Dynamic Contact Angles Measured in the Quartz-Dodecylammonium Chloride Solution System

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THESES FROM GRANT

The following masters theses have resulted from work carried out under this grant:

N. Gjelsvik, Streaming Potential Studies of the Kaolinite-Water Interface, M. S. Thesis, South Dakota School of Mines and Technology (1965).

W. W. Wen, Adsorption of Surfactants on Kaolinite, M.S. Thesis, South Dakota School of Mines and Technology (1966).

I. K. Choi, Effects of a Condensed Phosphate and a Long Chain Alcohol on Adsorption of Ionic Alkyl Surfactants onto Kaolinite, M.S. Thesis, South Dakota School of Mines and Technology (1966).

Y. Narimatsu, Streaming Potential and Microelectrophoresis Study of the Zeta Potential of Kaolinite in the Presence of Alkyl Ionic Surfactants, M.S. Thesis, South Dakota School of Mines and Technology (1966).

PUBLICATIONS FROM GRANT

The following publications have resulted wholly or in part from work carried out under this grant:

N. Gjelsvik and R. W. Smith, "Streaming Potential Studies in Quartz-Water and Kaolinite-Water Systems", Proc. S. D. Acad. Sci. Vol 44, p. 97 (1965).

R. W. Smith and W. W. Wen, "Adsorption of Cationic and Amine Surfactants on Kaolinite", 27th Ann. Min. Sym. Vol. of the U. of Minn., p. 193 (1966).

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R. W. Smith and R. W. M. Lai, "On the Relationship between Contact Angle and Flotation Behavior", paper in press, to be published in Trans. AIME.

In addition, the following paper will be presented at the Feb., 1967, AIME Meeting in Los Angeles: "Effects of a Condensed Phosphate and a Long Chain Alcohol on Adsorption of Ionic Alkyl Surfactants onto Kaolinite."